









# ELEMENTS OF CHEMISTRY.



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THEORETICAL AND PRACTICAL,

BY

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# PART II.

## INORGANIC CHEMISTRY.

### CHAPTER I.

#### INTRODUCTORY.

#### *Principles of Chemical Nomenclature.*

(281) Before proceeding to a description of the chemical properties of the different elementary substances, and of the compounds which result from their union with each other, it will be needful to explain the principles upon which the nomenclature in use amongst chemists has been founded. The object of the inventors of this language was, not merely to give a distinguishing name to the substances spoken of, but also to convey a knowledge of their components, and even of the proportions in which those components occur. In the less complicated substances with which the chemist has to deal, this object is very completely attained. In those of a more complex nature, the employment of symbols (15) becomes necessary, in order to enable the composition of the body to be fully indicated, and the *formula* of a substance, especially if the substance be derived from the animal or vegetable kingdom, becomes a necessary supplement to its name.

1. *Elements*.—In the case of the elementary bodies, the chemical name of each is usually that by which it is distinguished in common language, if the substance—as is the case with many of the metals, such as lead, iron, copper, or zinc—be one which is familiarly known: if it be a body which the researches of the chemist have brought to light, the name is generally indicative of some marked peculiarity by which the element is characterized. Thus phosphorus ('the light bearer') is so named because when exposed to the air it emits a feeble light which is visible in a darkened room; iodine derives its name from the violet colour of its vapour.

Hydrogen ('producer of water'), from the circumstance that it is a necessary component of water; and so on.

The attempt to introduce a strictly systematic nomenclature for the elementary substances has failed, owing to the strong hold which the popular names of those in familiar use have retained upon the language; but in the case of the more recently discovered metals a common termination in *um* has been assigned to them, as, for example, palladium, iridium, osmium, potassium, sodium, aluminum, &c. Among the non-metallic elements analogies are also pointed out, by a similarity in the termination of the name: thus, chlorine, iodine, bromine, and fluorine, have similar properties; and the existence of a certain analogy between boron and silicon is indicated by the common termination of both.

2. *Binary Compounds*.—When elements combine with each other to form a binary compound, that is to say, a compound in which two elements only are present, and in which also one equivalent (11) only of each substance is concerned, the nature of both the components is specified by the name employed; the name of the electro-negative ingredient (229), being that which is placed first as the generic term, whilst that of the electro-positive element follows as indicating the species; for instance, a combination of oxygen with zinc is designated oxide of zinc, the electro-negative element oxygen standing first and undergoing a modification or inflection in its name. The following table will illustrate the manner in which such modifications are applied; the symbols of the different compounds are given in the fourth column. It is to be observed that in employing symbols the rule observed as to the order in which the elements are arranged is the reverse of that which is adopted in the application of the name, for in the symbol the electro-negative element is always placed last:—

The compounds of	Are termed;	For Example:—	Or in symbols.
Oxygen	Oxides	Oxide of zinc	Zn O
Chlorine	Chlorides	Chloride of silver	Ag Cl
Bromine	Bromides	Bromide of sodium	Na Br
Iodine	Iodides	Iodide of potassium	K I
Fluorine	Fluorides	Fluoride of calcium	Ca F
Nitrogen	Nitrides	Nitride of boron	B N
Carbon	{ Carbides or Carburets }	Carbide of iron	Fe C
• Sulphur	{ Sulphides or Sulphurets }	Sulphide of copper	Cu S
	{ Sulphides or Sulphurets }	Sulphuret of lead	Pb S
Selenium	{ Selenides or Seleniurets }	Selenide of mercury	Hg Se
	{ Selenides or Seleniurets }	Seleniuret of cadmium	Cd Se
Phosphorus	{ Phosphides or Phosphurets }	Phosphide of hydrogen	H P
	{ Phosphides or Phosphurets }	Phosphuret of calcium	Ca P

3. *Multiple Compounds*.—It often happens, however, in consequence of the operation of the law of multiple proportions (10), that the same pair of elements forms two or more compounds endowed with different properties, and which contain different proportions of their components: the electro-negative element in this case is usually the one in which the multiple relation is observed; and the number of equivalents in which it enters into combination in the particular case is indicated by prefixing to the name an abbreviation of the corresponding Greek ordinal: *πρωτος* first, *δευτερος* second, *τριτος* third, &c. For example, there are four different oxides of osmium:

The first or lowest oxide is termed the protoxide of osmium	. .	Os O
The second oxide	„	deutoxide of osmium . . Os O <sub>2</sub>
The third oxide	„	tritoxide of osmium . . Os O <sub>3</sub>
The fourth oxide	„	tessaroxide, or peroxide of osmium . . . . } Os O <sub>4</sub> , &c.

Sometimes the Latin prefixes are substituted for those derived from the Greek: thus the terms *dinoxide* or *deutoxide* of nitrogen are used indifferently for a combination (NO<sub>2</sub>) of one equivalent of nitrogen and two equivalents of oxygen. In the same way the tetrachloride of antimony (Sb Cl<sub>4</sub>) is used as synonymous with the tritochloride of antimony. The highest oxide, chloride, or sulphide, is frequently termed the peroxide, perchloride, or persulphide. Thus the compound Mn<sub>2</sub> Cl<sub>7</sub> is termed the perchloride of manganese: CaS<sub>5</sub> is termed indifferently the persulphide or the pentasulphide of calcium.

4. *Acids*.—If the oxides possess acid characters, as, for example, is the case with some of the higher oxides of nitrogen, a different plan is adopted to mark this important peculiarity. At the time that the nomenclature was devised, oxygen was considered to be the element upon which the existence of the acid character mainly depended, as indeed its name (signifying ‘generator of acids’) implies. The system of nomenclature was therefore specially adapted to this idea. It frequently happens that an element forms more than one acid with oxygen: the compound which contains the largest proportion of oxygen is in this case indicated by making the name terminate in the syllable *ic*. Nitric acid (NO<sub>5</sub>), for instance, is the acid of nitrogen in which the largest quantity of oxygen is found: in like manner sulphuric acid (SO<sub>3</sub>) is the most highly oxidized acid of sulphur. A second acid which contains the same elements united with a smaller proportion of oxygen receives a name which ends with the syllable *ous*: thus nitrous acid (NO<sub>3</sub>) and sulphurous acid (SO<sub>2</sub>) indicate acids in which a smaller proportion of oxygen is present than in nitric and sulphuric acids.

When an acid exists in which a still smaller proportion of oxygen is present, the prefix *hypo*—from  $\upsilon\pi\omicron$ , 'below,' is usually employed; hyposulphurous acid ( $S_2O_2$ ) is the term employed to designate an acid which contains still less oxygen than sulphurous acid. Now and then an acid is discovered which contains still more oxygen than the one to which the termination *ic* has been appropriated. Chloric acid, for example, is represented as  $ClO_5$ , but an acid was subsequently found to exist, which has the composition  $ClO_7$ ; in this case the prefix *per* (which is an abbreviation for  $\pi\epsilon\rho$ , or *super*, 'above') is employed, the new compound having been termed perchloric acid.

The progress of research, however, has revealed other acids in which oxygen is wanting, but which contain hydrogen in its stead. These acids are usually distinguished by prefixing the word *hydro*, as an abbreviation for hydrogen: thus chlorine and hydrogen form an acid,  $HCl$ , hydrochloric acid, often called muriatic acid. Cyanogen and hydrogen form hydrocyanic or prussic acid,  $HCy$ , and so on. Many French writers, following Thénard, transpose these terms: they speak of chlorhydric acid, and cyanhydric acid. There is an advantage in this alteration, as it avoids any ambiguity which might arise from the use of the prefix *hydro*, which has sometimes been applied to compounds which contain water.

5. *Salts*.—When the acids unite with bases to form salts, the degree of oxidation in the acid is still indicated by the name of the salt. The name of the acid stands first as generic, the name of the base being added to show the species.

When acids ending in *ic* form salts, the termination of the acid is changed into *ate*: thus the salt formed when nitric acid unites with lime is termed nitrate of lime ( $CaO, NO_5$ ). When sulphuric acid combines with oxide of iron, the salt is called sulphate of oxide of iron, or usually, for the sake of brevity, sulphate of iron ( $FeO, SO_3$ ). Perchloric acid with potash forms the salt called perchlorate of potash ( $KO, ClO_7$ ). If the name of the acid end in *ous*, the termination is changed to *ite* in naming the salt: thus sulphurous acid and baryta form a salt called sulphite of baryta ( $BaO, SO_2$ ). Hyposulphurous acid and soda by their union form hyposulphite of soda ( $NaO, S_2O_2$ ).

It may here be well to caution those who are just commencing the study of chemistry of the necessity of distinguishing clearly between compounds, such as the sulphites and the sulphates, or the sulphides and the sulphites. Sulphide of sodium, for example, is a binary compound,  $NaS$ , containing a direct product of the

combination of two elementary substances, whereas sulphite of soda is a more complex compound ( $\text{NaO}, \text{SO}_2$ ), formed by the union of two compound bodies with each other. Sulphate of soda ( $\text{NaO}, \text{SO}_3$ ), again, contains an equivalent more of oxygen than the sulphite of this base.

If more than one equivalent of an acid be united with one equivalent of a base, there is no difficulty in pointing this out in the name. A compound of one equivalent of chromic acid and of potash ( $\text{KO}, \text{CrO}_3$ ) would be spoken of simply as chromate of potash; but there is another compound of potash with chromic acid in which two equivalents of the acid are present to one of the base; this compound is known as the bichromate of potash ( $\text{KO}, 2\text{CrO}_3$ ), the circumstance of the additional equivalent of acid being in this and in other analogous cases indicated by the prefix *bi*, from the Latin *bis*, 'twice,' which is made to precede the name appropriated to the neutral salt. The more complicated relation of three equivalents of acid to two of base, or the proportion of  $1\frac{1}{2}$  to 1, is expressed by the prefix *sesqui*, which means 'one and a half;' thus the compound of ammonia with carbonic acid, which forms the usual smelling salts, is called sesquicarbonate of ammonia ( $\text{HO}, 2\text{H}_4\text{NO}, 3\text{CO}_2$ ).

Occasionally it happens that it is the base instead of the acid which increases in multiple proportion. Some of the salts of lead exhibit this mode of combination; in such a case the nature of the compound is indicated by using the prefixes *di* or *dis*, for two equivalents of base, *tri* or *tris*, for three equivalents, and so on; ( $2\text{PbO}, \text{NO}_5$ ) would be dinitrate of lead, ( $3\text{PbO}, \text{C}_4\text{H}_3\text{O}_3$ ) triacetate of lead, &c.

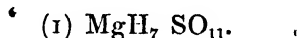
Generally speaking, a metal forms only one salifiable oxide, that is to say, only one oxide which has the power of combining with acids, and thus forming salts: but there are several exceptions to this rule. Iron, for example, may form salts in which the protoxide ( $\text{FeO}$ ) is present. Such salts are commonly distinguished as protosalts. ( $\text{FeO}, \text{SO}_3 + \text{HO}, 6\text{aq}$ ) represents the composition of the crystallized sulphate of protoxide of iron, and it is often described briefly as protosulphate of iron; but there is another series of salts of iron, in which the peroxide or sesquioxide ( $\text{Fe}_2\text{O}_3$ ) of the metal is the base; these are distinguished as the persalts, or sesquisalts, of iron: ( $\text{Fe}_2\text{O}_3, 3\text{SO}_3$ ) represents the sulphate of the peroxide (or sesquioxide) of iron, and it is usually termed the persulphate, or sesquisulphate of iron. These terms, although in general use, are not free from ambiguity.

Berzelius preferred to call the protoxide of iron, ferrous oxide, and the protosulphate, ferrous sulphate, whilst the sesquioxide he termed ferric oxide, and the sesquisulphate upon his plan was called ferric sulphate. This form of nomenclature, however, does not assimilate well with our language, though it has the advantage of brevity and precision.

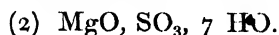
Other forms of nomenclature are applied in particular cases, but these will be best explained as the examples to which they refer arise.

(282) *Empirical and Rational Formulæ*.—In expressing the composition of a body by the use of symbols, the chemist may either content himself with simply stating the result of analysis by a mere enumeration of the elements and the relative number of equivalents of each; in which case he gives what is termed the *empirical formula* of the body; or he may attempt an explanation of the mode in which he conceives those elements to be associated together, and by the arrangement of his symbols may give expression to a theory of the composition of the body, and thus assign to it a *rational formula*. A body can have but one empirical formula, but it may be represented by a variety of rational formulæ, according to the different views which may be taken as to the mode in which its components are arranged.

Crystallized sulphate of magnesia, for example, has the following empirical formula:—



That is to say, it contains 1 equivalent of magnesium, 7 of hydrogen, 1 of sulphur, and 11 of oxygen. It is, however, never so written. The water which it contains may be entirely driven off by a heat a little above  $400^\circ \text{F.}$ ; and it is usually represented as consisting of magnesia, sulphuric acid, and water, as these are the materials out of which it is formed: thus—

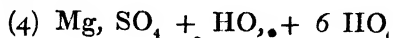


But it is found that at a heat of  $212^\circ$ , 6 equivalents of the water may be expelled, whilst the 7th equivalent requires a much higher temperature, so that it appears to occupy a position in the salt different from that of the other 6: this fact may be indicated by slightly altering the second formula.



Some chemists, however, guided partly by the results of the electrolysis of the salt, suppose that when once an acid and a base have united, their elements are arranged in different order to that

in which they existed when separate, and they prefer to represent the salt accordingly, as



Each of the last three formulæ is a rational formula for sulphate of magnesia; and each conveys far more information than the formula No. 1. Each represents a theory founded upon particular modes of decomposition which the salt may be made to experience.

It is impossible that all these formulæ should truly indicate the molecular constitution of the salt, though under particular circumstances they may represent the grouping of its component elements. Rational formulæ are indeed indispensable as the exponents of the theories which guide the chemist in his researches, or which aid him in arranging and interpreting phenomena; but, like the theories which they represent, they are but temporary expedients, and they must consequently always be regarded as such, and must be modified or discarded when they no longer faithfully represent the conditions of our knowledge of the compound which they are employed to indicate.

(283) *General Arrangement of the Elements adopted in this Work.*—The general division of the elementary bodies into non-metallic and metallic has been already pointed out. There is, however, no strict line of demarcation between the non-metallic and the metallic elements.

The bodies which are considered as non-metallic constitute the electro-negative ingredient in the binary combinations which they form with the metals, and are most of them insulators of the voltaic current. Carbon and silicon, however, in certain forms, act as conductors of electricity. The compounds of the non-metallic elements with oxygen generally show but little tendency to unite with acids; on the contrary, the higher oxides of most of them form powerful acids as the result of their combination with oxygen. These acids, except in the case of the silicic, dissolve readily in water; and even silicic acid, in certain cases, may be obtained in solution.

The metals, on the other hand, are characterized by a peculiar combination of opacity and compactness, which gives them, when polished, a peculiar brilliancy which is termed metallic lustre; they are good conductors of heat and electricity, and most of them, by combination with oxygen, form powerful bases. It is, nevertheless, sometimes difficult to determine whether a body be metallic



or not. Arsenic has a high metallic lustre; but it is more closely allied to phosphorus than to any other elementary substance, and both its oxides are endowed with well-marked acid properties. Tellurium, also, exhibits the closest analogy with selenium and with sulphur, but it possesses high lustre, and some conducting power for electricity.

The subdivision into non-metallic and metallic bodies is, however, convenient to the student, and it will therefore be retained in this work. The order in which the different elementary bodies will be treated is not in all cases that which a rigid adherence to analogy indicates, though this has generally been adopted. This order has, however, been departed from where it seemed more advantageous to the student to adopt a different course. In most cases we shall first examine the chemical properties which are exhibited by each of the elements in its uncombined form: we shall then study the general nature of its actions upon other elements, and shall afterwards examine the more important compounds into the formation of which it enters.

The most convenient and natural arrangement to adopt in the description of the properties of the non-metallic elements appears to be to consider first the four elements which enter into the composition of those all-pervading, and all-important substances, air and water, and then to pass on to others, classing them together according to the general analogy of their properties. Following this plan we shall consider first the properties of,

- |                                  |                                |
|----------------------------------|--------------------------------|
| 1. Oxygen                        | 3. Hydrogen (and water)        |
| 2. Nitrogen (and the atmosphere) | 4. Carbon (and carbonic acid.) |

Having examined some of the more important compounds which these bodies form with each other, we shall describe the well-marked natural group consisting of what Berzelius terms the Halogens, from the circumstance of their forming with the metals saline compounds resembling common salt—viz.

- |            |             |
|------------|-------------|
| 5 Chlorine | 7 Iodine    |
| 6 Bromine  | 8 Fluorine. |

Three combustible elements will be taken next in order—viz.,

- |                       |                |
|-----------------------|----------------|
| 9 Sulphur             | 11 Phosphorus; |
| 10 Selenium.          |                |
| 12 <del>Silicon</del> |                |

and the general survey of the non-metallic elements will be completed with

- |            |  |           |
|------------|--|-----------|
| 12 Silicon |  | 13 Boron. |
|------------|--|-----------|

For the convenience of description and of reference, the metals may be arranged in seven groups in the following order. The elements which compose each group generally present some natural resemblance, though, as already stated, the classification does not in all cases bring together those which, in chemical habitudes, are really the most closely allied. Some further remarks upon the analogies of the different elements will be offered when the principles which aid in determining the chemical equivalents are explained.

I. *Metals of the Alkalies*—3 in number.

	Oxides.	
1. Potassium . . . . .	Potash,	(KO).
2. Sodium . . . . .	Soda	(NaO).
3. Lithium . . . . .	Lithia	(LiO).

II. *Metals of the Alkaline Earths*—4 in number.

	Oxides.	
1. Barium . . . . .	Baryta	(BaO).
2. Strontium . . . . .	Strontia	(SrO).
3. Calcium . . . . .	Lime	(CaO).
4. Magnesium . . . . .	Magnesia	(MgO).

III. *Metals of the Earths*—10 in number.

	Oxides.	
1. Aluminum . . . . .	Alumina	(Al <sub>2</sub> O <sub>3</sub> ).
2. Glucinum . . . . .	Glucina	(Gl <sub>2</sub> O <sub>3</sub> ).
3. Zirconium . . . . .	Zirconia	(Zr <sub>2</sub> O <sub>3</sub> ).
4. Thorium . . . . .	Thorina	(ThO).
5. Yttrium . . . . .	Yttria	(YO).
6. Erbium . . . . .	Erbia.	
7. Terbium . . . . .	Terbia.	
8. Cerium.		
9. Lanthanum.		
10. Didymium.		

IV. *Metals more or less analogous to Iron*—8 in number.

1. Zinc.	5. Uranium.
2. Cadmium.	6. Iron.
3. Cobalt.	7. Chromium.
4. Nickel.	8. Manganese.

V. *Metals which yield Acids*—11 in number.

1. Tin.	7. Tungsten.
2. Titanium.	8. Vanadium.
3. Columbium.	9. Antimony.
4. Niobium.	10. Arsenic.
5. Ilmenium.	11. Tellurium.
6. Molybdenum.	

VI. 3 *Metals*.

1. Bismuth.	3. Lead.
2. Copper.	

VII. *Noble Metals*—9 in number.

1. Mercury.	6. Rhodium.
2. Silver.	7. Ruthenium.
3. Gold.	8. Osmium.
4. Platinum.	9. Iridium.
5. Palladium.	

## CHAPTER II.

## THE ATMOSPHERE.

(284) *Compound Nature of the Atmosphere*.—The chemical researches of the philosophers of the last century are especially remarkable on account of the important information which they afforded upon the nature of the atmosphere. Indeed, the knowledge thus obtained may be regarded as the starting point of the brilliant chemical discoveries which have since succeeded each other with such rapidity.

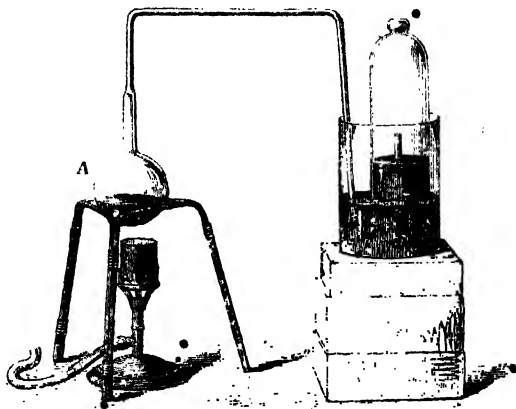
These researches have abundantly proved that the air is far from being, as it was once supposed to be, an elementary body. It has been found, on the contrary, to be a mixture of several substances, some of which are elementary, others compound.

The most remarkable and abundant of the constituents of the air are the elementary bodies, oxygen and nitrogen; and of its compound ingredients aqueous vapour and carbonic acid are the most important.

The most direct proofs of the compound character of the atmosphere are afforded by examining the effects produced in it by burning bodies. Bodies, as is well known, cannot burn without the free access of air. On placing a lighted taper under the receiver of the air-pump and exhausting the air, the flame becomes extinguished. A limited quantity of air will only support combustion for a limited period: a lighted taper floating on water under an inverted bell-glass, the edge of which is plunged beneath the water, soon begins to burn dimly, and at length becomes extinct. But the taper ceases to burn long before the air is all spent. The receiver still contains a large quantity of a gaseous body in which a candle will not burn. The results obtained by burning a candle in a limited portion of air are however rather complicated, because the products which are formed by the burning body rise in the form of gas, and mix with the remaining portion of air. In a form of experiment which was devised by Lavoisier during his researches upon the atmosphere, he contrived to obviate this inconvenience by acting upon the air with a substance which produced a solid body as the result of the chemical action, and left the air unmixed with any gas which rose from the burning body. The substance which he employed to decompose the air was metallic mercury, a substance which acts very slowly, and which does not appear to burn in the ordinary sense of the term. The experiment may be performed as follows:—

Into the bulb of a flask or retort (A, fig 224), provided with a neck of considerable length, an ounce or two of metallic mercury is introduced: the neck of the flask is then bent in the manner shown in the figure, and the bent portion plunged into a mercurial bath, so as to leave the open end of the neck projecting above the level of the mercury, into a jar partially filled with atmospheric air. The bulk of this portion of air

FIG. 224.



is accurately observed, and the temperature and barometric pressure at the time of the observation are recorded. Heat is now applied to the flask, and maintained steadily at a point just below that required to make the mercury boil. If this temperature be continued for three or four consecutive days, the decomposition of the air inclosed both in the flask and in the jar will be effected. The mercury will gradually become covered with red scales, and the air in the jar, which at first expanded from the action of the heat, will slowly decrease in bulk until fresh scales no longer continue to be formed. When this point is reached the source of heat may be removed, and the remaining air, when cold, will be found to measure nearly  $\frac{1}{4}$ th less than it did at the commencement. If a portion of this residual air be decanted into another jar it will be found to be unfit for the support of animal life; a mouse or other small animal introduced into it speedily dies, and the flame of a candle is instantly extinguished. The gas which has been thus obtained, is an elementary body nearly in a state of purity, it is termed nitrogen ('generator of nitre'), as it forms an essential constituent of nitre or saltpetre; occasionally it is distinguished by the name of azote, from its inability when pure to support life, although it is not directly poisonous. In this experiment the heated mercury has been slowly effecting the removal of the oxygen from the air.

### § I. OXYGEN.

*Symbol, O; Equivalent, 8; Combining Volume, 1; Specific Gravity, 1.1057.*

(285) If in the foregoing experiment, the red scales which formed upon the mercury when it is heated in a confined portion of air, be introduced into a small retort and exposed to a strong heat, they will gradually disappear; drops of mercury will condense in the cool part of the retort, and a gas will be disengaged, which may be collected over water. If the experiment be performed with sufficient accuracy the quantity of the gas obtained will be exactly equal in volume to the bulk absorbed from the air by the mercury.

To this gas the name of Oxygen has been given. It is an elementary body, and ranks indeed among the most remarkable and important of all the elements.

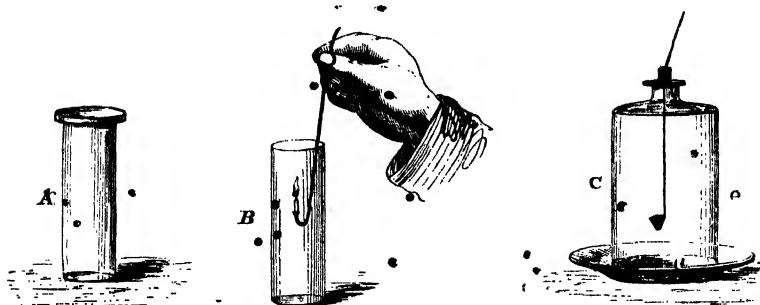
*Properties.*—Oxygen gas possesses the power of supporting com-

bustion in an eminent degree. If a splinter of wood with a glowing spark on any part of it be plunged into the gas, the wood will instantly burst into flame, and will burn with extraordinary brilliancy. A small animal will live in a confined space filled with oxygen for a longer period than in an equal bulk of air; but the gas is of too stimulating a quality to be breathed undiluted with impunity for any considerable time, and before long it produces death from over-excitement of the system.

Oxygen, like air, is destitute of colour, taste and smell. Of all known substances it has the smallest refracting power for the rays of light. Hitherto all attempts to reduce it to the liquid form by the combined application of pressure and of cold have proved fruitless. Oxygen has been proved to possess weak but decided magnetic properties, like those of iron, and like this substance its susceptibility to magnetization is diminished, or even temporarily suspended, by a sufficient elevation of temperature (275). According to Regnault, 1 litre, (61.024 cub. in.) at 32° F., Bar. 29.922, weighs on a mean of three very careful experiments, 1.4298 grammes. This reduced to the English standard of 60° F. and 30 inches Bar., gives 34.203 grains as the weight of 100 cubic inches of oxygen. It is heavier than the atmosphere, its specific gravity, deduced from the experiments just mentioned, being 1.10563;\* and it is only slightly soluble in water, which takes up about  $\frac{1}{30}$ th of its bulk. Oxygen is essential to the support of animal life, and hence by the older chemists was termed *vital air*. Oxygen possesses extremely powerful chemical affinities for other elements, one only (fluorine) being known with which it does not combine and form compounds. Owing to the intensity with which many of these actions take place, bodies which burn tranquilly in air often deflagrate with violence in oxygen. Phosphorus burns in it with a brilliancy which is painful to the eye; many metals also burn vividly in it: a piece of potassium the size of a pea, placed in a small copper spoon, c, fig. 225, and heated strongly by a spirit lamp, bursts into flame when plunged into the gas; if a piece of German tinder be attached to a piece of thin iron wire and be lighted, to start the combustion before it is introduced into the oxygen, the wire will burn with brilliant scintillations; zinc foil burns in oxygen with an intense bluish white light; and in like manner sulphur and charcoal, if previously kindled, also burn in the gas with great vehemence.

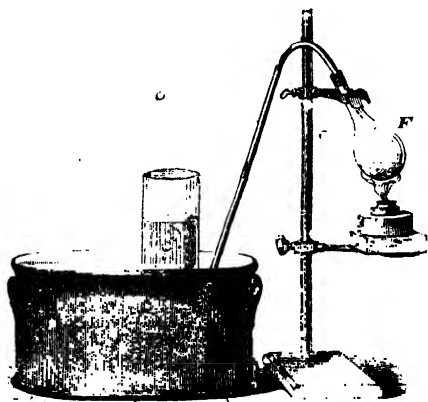
\* Dumas and Boussingault found the density of oxygen almost exactly the same as that given above—viz. 1.1057: Saussure states it to be 1.1056.

FIG. 225.



*Preparation.*—Although oxygen was first obtained by Priestley, in 1774, by the action of heat upon the red oxide of mercury, there are other methods of procuring it which are more convenient and economical. Many substances which contain oxygen part with it on the mere application of a strong heat: chlorate of potash is

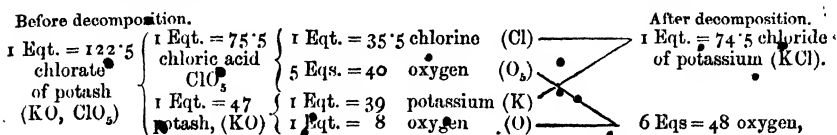
FIG. 226.



one of these; 200 or 300 grains of this crystallized salt may be heated over a gas flame or a charcoal fire, in a green glass retort or in a Florence flask, *F*, (fig. 226), furnished with a cork which is adapted to a bent tube for delivering the gas; the salt fuses at a heat below redness, and at a temperature a little above its melting point emits a large quantity of gas, which may be collected in jars over

water in the pneumatic trough, or it may, if not wanted for immediate use, be stored up in a gas-holder (38). If a jar of the gas be closed with a glass plate it may readily be inverted, as at *A*, fig. 225, and its power of supporting combustion tested by a taper, as shown at *B*. The oxygen furnished by chlorate of potash is perfectly pure, and amounts to more than one-third of the weight of the salt used; 1 ounce of the crystals should yield about 512 cubic inches, or nearly 2 gallons of the gas. Chlorate of potash is a compound of chloric acid with potash; the chloric acid consists of oxygen and chlorine; the potash, of oxygen and potassium;

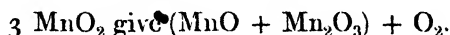
both the chloric acid and the potash, when heated together, are decomposed, and give up all their oxygen in the gaseous form, whilst the chlorine and potassium unite and constitute the white salt which remains in the retort when the operation is over. The following diagram may assist in explaining these effects :—



Or in symbols :  $\text{KO, ClO}_5 \text{ yield KCl} + \text{O}_6$ .

When the quantities of chlorate employed are rather large, the heat required is apt to soften the glass of the flask in which it is decomposed, and it is needful to employ a stronger heat than a lamp will easily furnish. It has, however, been found that many metallic oxides, if mixed in fine powder with the pulverised chlorate in a proportion of not less than one part to ten of the salt, cause the expulsion of the gas at a much lower temperature, ranging between  $450^\circ$  and  $500^\circ$  F., although such oxides have not been proved to experience any chemical change during the operation. It is therefore convenient in practice to mix the chlorate of potash with about a fourth of its weight of black oxide of copper ( $\text{CuO}$ ) or of manganese, that has been previously heated to redness and allowed to cool. The gas which is obtained in this way is, however, apt to contain traces of chlorine.

For the supply of large quantities of oxygen it is usual to employ the black oxide of manganese ( $\text{MnO}_2$ ), a mineral found abundantly in Devonshire and in various other parts of the world. At a red heat it parts with one-third of the oxygen which it contains, whilst a reddish brown oxide of manganese remains behind. This decomposition is expressed in symbols as follows :



The mineral must be reduced to small fragments about the size of a pea, and introduced into an iron bottle, fig. 227, to the neck of

FIG. 227.



which an iron pipe is fitted by grinding; the bottle is heated in a furnace, and the gas is conveyed to the gas-holder by means of a



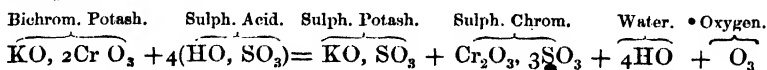
piece of flexible metallic piping of suitable length. As the oxide of manganese usually contains a portion of water, and frequently also some carbonate of lime, the first effect of heat is to drive off a quantity of steam mixed with a gas which consists principally of carbonic acid. When the gas that comes off rekindles a glowing match, it may be collected for use. Oxide of manganese, when chemically pure, furnishes about  $\frac{1}{8}$ th of its weight of oxygen; but as met with in commerce it seldom yields more than half this quantity, a pound giving off about 1400 cubic inches of the gas.

Oxygen may be obtained from various other substances, but those already mentioned are the best, and are the materials most frequently employed. Red lead, as well as saltpetre, when heated strongly, furnishes the gas; and a mixture of sulphuric acid in its concentrated form with half its weight of powdered oxide of manganese, or of bichromate of potash, may also be made use of by applying heat to the materials placed in a glass retort.\*

(286) *Nature of Combustion.*—The distinguishing feature of oxygen is its remarkable power of supporting combustion. Whenever any rapid chemical action attended with extrication of light and heat takes place, *combustion* is said to 'occur'. In order to commence this action it is generally necessary to apply heat; afterwards the heat which is liberated during the process is more than sufficient to carry it on, and the act of combination proceeds with increasing rapidity. • A stick of charcoal may be kept in oxygen at common temperatures for years without entering into combination with the gas, but the smallest spark upon the surface of the charcoal will suffice to determine its immediate and vivid combustion.

It must ever be borne in mind that in the case of combustion, as in every instance of chemical action, how completely soever the combustible, or body which is burned, may change its form so as

\* Bichromate of potash and sulphuric acid when heated together undergo a decomposition, in consequence of which, oxygen, sulphate of potash, and sulphate of chromium are produced. This change may be represented in the following manner:—

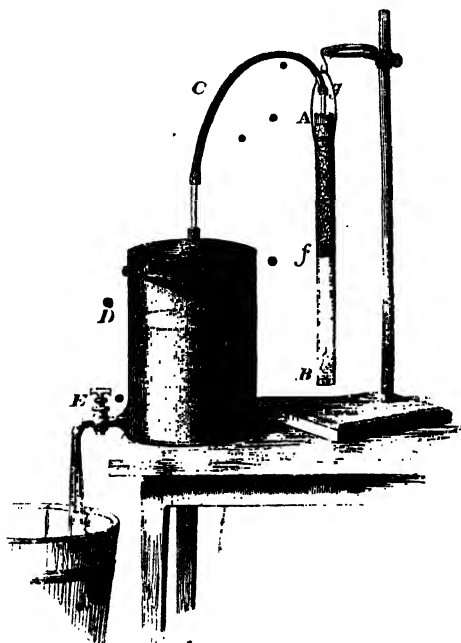


Part of the sulphuric acid is employed in displacing the chromic acid from the bichromate of potash, and in forming sulphate of potash in its place, whilst another portion of the sulphuric acid assists in decomposing the liberated chromic acid, which loses half its oxygen and becomes converted into oxide of chromium, and this oxide, by combining with the sulphuric acid, forms sulphate of chromium.

even to disappear from our sight, there is no actual destruction of matter, or loss of weight. A candle in burning seems to disappear completely; and when the combustion is over an insignificant trace of ash from the wick is all that remains to the eye. It is, however, easy to show that nothing is destroyed in this operation, but that the constituents of the candle in burning have combined with a certain proportion of oxygen, and that the acriform compounds, carbonic acid and aqueous vapour, which are the result of the combustion, though invisible, really weigh more than the original candle; the gain in weight representing the quantity of oxygen which by its combination with the materials of the candle has produced the chemical change.

FIG. 228.

The experiment may be conducted in the following manner:—Take a glass tube, *A B*, fig. 228, 14 or 15 inches long, and  $1\frac{1}{4}$  inch in diameter; thrust a piece of wire gauze, *f*, half way down the tube, and fill the upper half with fragments of fused potash. The fused potash is employed to retain both the carbonic acid and the moisture, which are the only compounds produced by the burning candle, if it be properly supplied with air. To the lower end of the tube fit a cork perforated with



three or four holes for the admission of air, and fasten to it a short piece of wax taper. To the other end of the tube adapt a sound cork, through which a short piece of tube, *g*, about one-third of an inch in diameter is passed. Now weigh the tube and its contents. Connect the tube *g* with a piece of flexible tubing, *c*, to an aspirator jar, *D*, filled with water; open the stopcock, *E*, and let the water flow. The water cannot escape at *E* till its place is supplied by atmospheric air; and since the aspirator, through the tube *c*, is connected with

A B, which at B communicates freely with the atmosphere, a current of air is established through A B. Now withdraw the cork B, light the taper, and quickly replace it in the tube; in about three minutes time close the stopcock of the aspirator: the taper is instantly extinguished. Detach the tube C, and when cold, the glass, A B, will weigh several grains heavier than before.

At the ordinary temperature of the atmosphere oxygen frequently enters slowly into combination without any perceptible disengagement of heat, as when a bar of iron is gradually rusting in the air. In other instances, where the process is more rapid, the heat accumulates, and sometimes it rises high enough to cause the materials to burst into flame, producing what are called cases of spontaneous combustion. Charcoal that has been reduced to fine powder preliminary to the manufacture of gunpowder, and which offers a large surface to the air, occasionally exhibits this phenomenon; and it is still more often manifested when tow that has been used for wiping machinery lubricated with oil is laid aside in heaps. The oil when spread over so large a surface, absorbs oxygen rapidly, and the temperature goes on rising until the mass bursts into flame.

The more the oxygen is diluted, whether by diminution of pressure, or by mixture with a gas which does not chemically act upon it, as with the nitrogen of the atmosphere, the less elevated is the temperature which is produced in a given time by combustion, because fewer particles are in contact with the burning body, and the more slowly, in consequence, does the operation proceed. The activity of the combustion is greatly increased by increasing the number of particles of oxygen which are brought in a given time into contact with the combustible, and by carrying away the gaseous products of combustion which are incapable of combining with the fuel, and which, if suffered to accumulate, would cut off the supply of fresh oxygen; in this way the action of the smith's bellows and the blowing machine of the blast furnace may be explained. The influence of a long chimney in producing a powerful heat in the furnace at its base is similar; whilst the effect of diminishing the supply of air by closing the damper, or shutting the door of the ash-pit is seen in the diminished temperature, and reduced consumption of fuel which occurs under such circumstances.

It is, however, important to remark that the quantity of heat emitted during the combination of a given quantity of oxygen is definite, and is dependent in part upon the chemical nature of the burning body, but it is independent of the rate at which the combustion is effected.

The act of respiration in animals, during which the oxygen of the air is brought into contact with the blood through the agency of the lungs, is attended with a slow change, analogous to combustion, and is accompanied by extrication of heat; an oxidation of part of the constituents of the blood occurs, and at the same time the colour of the blood is changed from a dusky purple to bright crimson.

All bodies may, with reference to combustion, be arranged under one of three classes. The first class consists of bodies which, like oxygen, allow other substances to burn in them freely, but which cannot themselves, in ordinary language, be set on fire: these are termed *supporters of combustion*. The second class consists of bodies which, like charcoal, actually burn, when sufficiently heated in a gas belonging to the first class: these substances are termed *combustibles*. The third class embraces such bodies as will neither burn themselves nor support the combustion of others; they may be made red hot, but do not burn; sand, iron-rust, and earthy bodies in general are examples of this kind: they are for the most part compounds that have at some time or other been produced by combustion; that is, they are bodies that have been already burned, and are no longer fitted to undergo this change.

The compounds which oxygen forms with other elements are in chemical language termed *oxides*, and a body which has combined with oxygen is said to be oxidized. The number and variety of these compounds are very great, for oxygen is the most widely diffused and abundant of the elements. It constitutes about a fifth in bulk of the atmosphere; it forms eight-ninths of all the water on the globe, and it is not less extensively met with amongst the solid constituents of the earth: silica, in all its varieties of sand, flint, quartz, rock crystal, &c.—chalk, limestone, and marble—and all the various forms of clay, each contain about half their weight of oxygen. In the form of animal and vegetable life it is also equally generally diffused; it is indeed absolutely essential to the maintenance of the vital functions in both; and although not the only body which is fitted to support combustion, it is, from its existence in the atmosphere, the element which, in the vast majority of cases maintains combustion on the surface of our planet.

(287) *Varieties of Oxides*.—Amongst the varied compounds formed by oxygen it is remarkable that there exist two classes which are in chemical properties directly opposed to each other. Many substances, like phosphorus, by their combination with oxygen, yield a compound which dissolves freely in water, has a

sour, burning taste, and turns many vegetable blue colours, such as the blue of an infusion of litmus or of purple cabbage, to a bright red, and which, in short, possesses the characters of an *acid*.

The name oxygen (from  $\alpha\acute{\xi}\upsilon\gamma\epsilon\varsigma$ , sour, and  $\gamma\epsilon\nu\nu\alpha\omega$ , to produce,) or 'producer of acids,' was given to the element from the circumstance of its entering into the formation of bodies which in so great a number of cases possess the acid character. All the elements which are not metallic, with the exception of hydrogen and of fluorine, form with oxygen one or more acid compounds. Most of the metals, however, by their union with oxygen, give rise to bodies of an opposite kind, which have been termed *bases*. Potassium, for example, when burned in oxygen, furnishes a white alkaline substance, which dissolves rapidly in water, and produces a colourless liquid, of a soapy disagreeable taste, and a peculiar lixivial smell; it has a caustic action on the skin, restores the blue colour to litmus which has been reddened by an acid, and it completely neutralizes the strongest acids. Other metals form oxides, which though not soluble in water, nevertheless preserve their basic character, and saturate the acids perfectly. Oxide of iron, for instance, dissolves in sulphuric acid, and forms with it a crystalline salt. It is found that when an element combines with oxygen to form an acid it unites with a larger number of equivalents of oxygen than when a base is the result of the combination.

Intermediate between the acids and bases is a third class of oxides, which are indisposed to enter into combination with either. The black oxide of manganese ( $\text{MnO}_2$ ), the magnetic oxide of iron ( $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ), and red lead ( $2\text{PbO}$ ,  $\text{PbO}_2$ ), may be mentioned as instances of this kind: such oxides are often produced by the union of two other oxides with each other.

The oxidation of the metals has been observed to take place much more rapidly in a moist than in a dry atmosphere. A bar of polished iron will remain in dry air unchanged for any length of time, but if moisture be present it will quickly become rusty; the oxide of iron in this case combines with the water which it absorbs from the air. In the case of iron, the oxidation continues to spread through the entire mass of the metal; but in other instances, as occurs with lead and zinc, a superficial coat of oxide is formed, which adheres firmly to the surface, and protects the metal beneath from further change.

(288) *Ozone*.—When a succession of electric sparks is transmitted through atmospheric air or through dry oxygen, a peculiar odour is perceived, which has by some been compared to that of weak chlorine. To the body which produces it Schoenbein gave

the name of *ozone*, from the circumstance of its possessing a powerful odour. Opinions upon the cause of this odour were long divided; but it has at length been proved, by the concurrent observations of several accurate experimentalists, to be owing to a modification produced in oxygen itself, by which it is made to assume a more active condition. One of the easiest methods of exhibiting this phenomenon consists in transmitting a current of pure dry oxygen through a tube into which a pair of platinum wires is scaled, with the points at a little distance apart. On transmitting a succession of electric sparks through the stream of gas as it issues, the peculiar odour of ozone is immediately developed. Notwithstanding the powerful smell thus produced, a minute portion only of the oxygen undergoes this change. The following are some of the characters which are exhibited by the altered portion:—

Ozone is insoluble in water, and in solutions either of acids or alkalis. It possesses considerable bleaching powers, acts rapidly as a powerful oxidizing agent, and corrodes organic matters, such as the cork or caoutchouc used in connecting the different parts of the apparatus together: fragments of iron, of copper, and even of silver when moistened, rapidly absorb ozone and become converted on their surface into oxides; silver even becomes a peroxide, though this metal is wholly unchanged by ordinary oxygen. Ozone displaces iodine from its combinations with the metals, setting the iodine at liberty; indeed, this reaction is so easily produced that it furnishes the readiest and most delicate method of detecting the presence of traces of ozone in the air; a slip of paper moistened with starch and iodide of potassium, and inserted into a vessel containing the smallest admixture of ozone, becomes blue from the action of the liberated iodine, which immediately unites with the starch, and forms the blue iodide of starch which is so characteristic of iodine. Paper soaked in solution of sulphate of manganese ( $MnO, SO_3$ ) likewise shows the presence of ozone by becoming brown, owing to the manganese which exists as protoxide in the sulphate assuming an additional equivalent of oxygen, and becoming converted into the peroxide. If the paper be stained black with sulphide of lead ( $PbS$ ), this stain will gradually disappear; both the sulphur and the lead will absorb the ozone, or active oxygen, and a white sulphate of lead ( $PbO, SO_3$ ) will be formed. One of the most singular circumstances connected with ozone is the effect of heat upon it. A temperature not much higher than that of boiling water is sufficient to destroy all its active character. By placing the flame of a spirit lamp so as to heat a part of the tube

through which the electrified oxygen escapes, all signs of ozone disappear.

Ozone may be obtained without the aid of electricity. If a stick of clean phosphorus, moistened with a few drops of water, be placed in a bottle of atmospheric air, the slow oxidation of the phosphorus is attended with the production of ozone: in an hour or two this attains its maximum. If the phosphorus be not then removed, the ozone by degrees disappears, owing to its combination with the phosphorus. It is also probable that ozone is formed in other slow oxidations, such as that of ether, and of oil of turpentine. The cause of this change in the properties of the oxygen in these cases is unknown. It was supposed that the peculiar odour which is frequently observed in oxygen obtained by the voltaic decomposition of acidulated water was due to ozone; but Baumert (Poggendorff's *Annal.* lxxxix. 38) seems to have shown that it arises not from oxygen, but, as supposed by Schönbein, from a volatile peroxide of hydrogen (probably  $\text{HO}_3$ ).

## § II. NITROGEN.

*Symbol, N; Equivalent, 14; Combining Volume, 2; Specific Gravity, 0.9713.*

(289) It has already been observed that the larger proportion of the atmosphere consists of a gaseous body, named nitrogen, which is incapable of supporting life. It is a colourless, tasteless, and inodorous gas, which as yet has resisted every effort to liquefy it. Nitrogen is somewhat lighter than atmospheric air, having a specific gravity of 0.9713. Calculating from Regnault's experiments, 100 cubic inches at 60° F. Bar. 30 in., weigh 30.119 grains. Water dissolves not more than  $\frac{1}{40}$ th of its bulk of this gas at ordinary temperatures, 100 cubic inches of water absorbing about  $2\frac{1}{2}$  cubic inches of nitrogen. No two substances can offer a more striking contrast in chemical properties than oxygen and nitrogen: the one the most energetic of the elements, the other the most indifferent. Though it extinguishes a taper without taking fire itself, and though an animal immersed in the undiluted gas quickly perishes for want of oxygen, it is not directly poisonous; indeed, it enters as a necessary component into the animal frame, and with every act of inspiration, it finds admission into the lungs. One very important purpose that it fulfils is the dilution of the oxygen, which is rendered thereby less stimulating to the living system, and the rapidity of ordinary combustion is likewise thereby moderated. It is indeed one of the most extensively diffused forms of matter, as must be

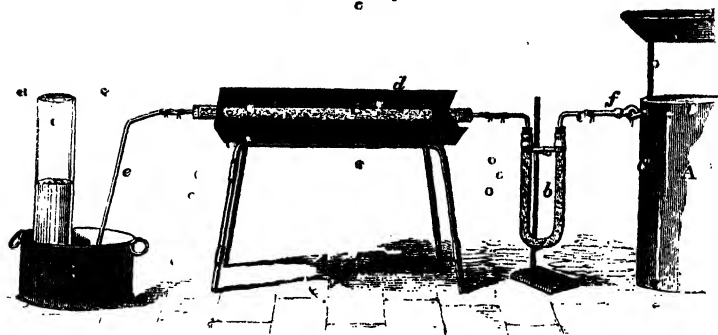
evident from the facts just stated; and notwithstanding its apparent indisposition to enter into combination, nitrogen forms a number of highly interesting and important compounds. In combination with oxygen, it forms nitric acid, which exists as a natural production when united with potash and soda in the nitrates of those bases; it is the characteristic ingredient in ammonia; and though it occurs in but small quantity in plants, it is rarely if ever entirely absent from them. In many of the most potent and valuable medicines, such as quinia and morphia, as well as in some of the most dangerous poisons, as prussic acid and strychnia, nitrogen constitutes an essential part.

*Preparation.*—The most convenient methods of preparing nitrogen are based upon the removal of oxygen from atmospheric air. The simplest plan consists in placing a few fragments of phosphorus, dried by means of blotting paper, on a porcelain dish, which is floated upon the surface of the water of the pneumatic trough; the phosphorus is ignited by touching it with a hot wire and a glass receiver filled with air is then inverted over it. The phosphorus burns at the expense of the oxygen in the confined air, and being partially converted into vapour by the heat which attends the combustion, is diffused through the gas, and thus quickly searches out and combines with every portion of oxygen: when cold, the nitrogen may be decanted into another jar and examined. The removal of oxygen from the air may also be effected more slowly in various ways; a stick of phosphorus will, if introduced into a jar of air which is standing over water, slowly absorb the oxygen, and in two or three days about four-fifths of the original bulk of the air, consisting of nitrogen nearly pure, will be left. Moistened iron filings produce a similar result, the metal gradually becoming oxidized, as is seen by the rusty appearance which it assumes. When larger quantities of nitrogen are required, metallic copper may be employed to absorb the oxygen. The method to be adopted in this case is exhibited in fig 229. *c* represents a long straight tube of hard glass, which will resist a strong heat without fusion; it is filled with metallic copper in a finely divided state; for this purpose the metal which has been reduced from the powdered oxide by means of hydrogen gas is well adapted. The tube *c* rests on a sheet-iron furnace, *d*, in which it can be surrounded by charcoal and raised to a red heat; *e* is a bent tube for delivering the gas into a jar over water or mercury; the other extremity of the tube *c* is connected with a bent tube, *b*, filled with fragments of fused caustic potash, and the air which supplies the nitrogen is driven from the gas-holder, *a*, over the



ignited copper in a stream which is easily regulated by the stop-cock, *f*. The air is first driven over the fused potash, where it

Fig. 229.



leaves all traces of carbonic acid and of moisture, it then passes through the ignited copper, by which every portion of oxygen is completely removed. Nitrogen may also be obtained by the action of chlorine on a solution of ammonia (325), and it is furnished in a state of equal purity by heating the nitrite of ammonia (311).

### § III. COMPOSITION OF THE ATMOSPHERE.

(290) If a mixture be made of 4 measures of nitrogen and 1 measure of oxygen gas, a candle will burn in it as in atmospheric air; it may be breathed as air, and in fact possesses the ordinary properties of the air. The atmosphere is in short a mechanical mixture of several gases, amongst which oxygen and nitrogen constitute the principal portion, and which, notwithstanding their difference in density, are, owing to the principle of diffusion (64), uniformly mixed with each other. Chemical operations are continually occurring upon the earth's surface, which remove oxygen and add a variety of other gases, amongst which carbonic acid is the most abundant. Yet so beautifully adjusted is the balance of chemical actions over the face of the earth, that no perceptible change in the composition of the atmosphere has been observed since accurate experiment on the subject has been practised.

Air which has been freed from carbonic acid and aqueous vapour consists, according to the numerous careful analyses of Dumas and Boussingault, on an average of 20.81 of oxygen by measure, and of nitrogen in 100.00 parts, or by weight of 23.01 of oxygen, and of nitrogen. These experiments were performed by allow-

ing the air to stream slowly over a weighed quantity of heated copper, whereby the oxygen was absorbed (fig. 229) whilst the nitrogen was received into an exhausted flask, which was weighed before the experiment was commenced and after its termination; the quantity of oxygen was found by the gain in weight experienced by the tube containing the copper. The results obtained by Regnault, Brunner, Verver, and others, by different methods of analysis do not vary more than  $\frac{1}{100}$  from the quantity of oxygen just mentioned; trifling temporary variations no doubt occur from local causes; but the air brought by Gay-Lussac from an elevation of four miles above the surface of the earth, that collected on the summit of the Alps, and that examined both in town and country in various parts of the globe, present no sensible difference from the mean above given.\*

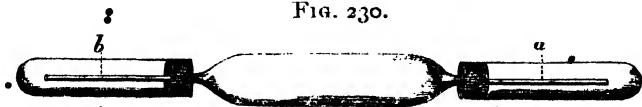
100 cubic inches of dry air weigh, at 60° F. and 30 inches Bar., calculating from the experiments

of Biot and Arago . . . . .	31·074	grs.
of Dumas and Boussingault . . . . .	31·086	„
of Regnault . . . . .	30·935	„
of Dr. Prout . . . . .	31·0117	„

The first result is probably the most accurate, as it exactly corresponds with the density deduced from that of a mixture of oxygen and nitrogen in the proportions in which they occur in the atmosphere. The weight of a given volume of air at 60° F.,

\* A portion of air collected by Mr. Welsh, in August, 1852, at an elevation of 18,000 feet, in one of the balloon ascents undertaken by him and Mr. Green under the direction of the Kew Committee of the British Association, contained 20·88 per cent. of oxygen by volume, while air collected at the surface at the same time contained 20·92. The air was collected in tubes of about 6 cubic inches in capacity, fitted with accurate stopcocks. They were exhausted previous to the ascent, and were filled with the air for examination by opening the stopcocks, which were again closed as soon as the charge had entered. In the extensive series of experiments of M. Regnault (*Ann. de Chimie*, III., xxxvi. 385), air was collected at different points of the earth's surface in glass tubes, drawn out to an open capillary extremity at either end, fig. 230. When a specimen of air was to be collected, one of these tubes was

FIG. 230.

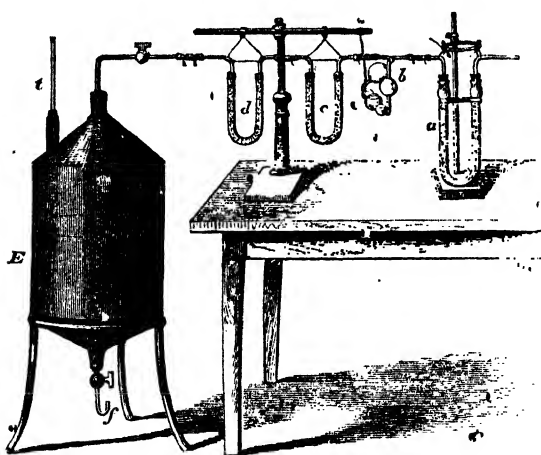


attached by a flexible tube to a small pair of bellows, and by working the bellows a few times, the tube was filled with air of the locality. The capillary tubes were then drawn off and sealed, as at *a* and *b*, by momentary contact with the flame of a spirit-lamp, and the closed ends were protected from injury during the journey by small caps of glass tube fitted with corks. The analyses of the air thus obtained were executed by means of hydrogen, in an eudiometer of Regnault's contrivance. The same apparatus was used by myself in the analyses of the air collected by Mr. Welsh.

under a pressure of 30 inches Bar<sup>t</sup>, is therefore only  $\frac{1}{11}$  of that of an equal bulk of water at the same temperature. Owing to the greater solubility of oxygen than of nitrogen, rain water and melted snow always contain a larger proportion of oxygen than the air itself, amounting to about 34 per cent. of the air dissolved, or nearly 2 parts of nitrogen to one part of oxygen. This is a circumstance of great importance to aquatic animals, and one which could occur only in consequence of the air being a mechanical mixture and not a chemical compound of the two gases. In addition to oxygen and nitrogen the atmosphere contains a certain proportion of carbonic acid; a variable but minute trace of ammonia; traces of nitric acid and of some compound of carbon and hydrogen, and frequently in towns a perceptible amount either of sulphurous acid or of sulphuretted hydrogen. Aqueous vapour is of course also present at all times, although its amount is liable to extensive fluctuations.

The amount of aqueous vapour at any spot may be ascertained

FIG. 231.



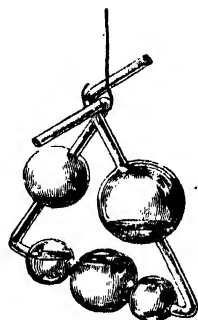
by means of the hygrometer (181), or it may be determined by a direct experiment in the following manner. A bent tube, *a*, fig. 231, filled with pumice stone moistened with sulphuric acid, is connected with a vessel, *e*, of known capacity; suppose it be capable of containing 18 gallons of water. This

vessel having been filled with water, is allowed slowly to empty itself by opening a stopcock, *f*, which terminates in a tube bent upwards to prevent the entrance of air at the bottom; a known volume of air is thus drawn through the tube *a*, which retains all the moisture. If the weight of this tube be determined before commencing the experiment, and a second time after it is completed, the increase in weight will indicate the amount of moisture in the bulk of air operated upon. The temperature is ascertained<sup>t</sup> by means of the thermometer, *t*, and the atmospheric pressure is obtained by an observation of the

barometer at the time. The flow of water from the aspirator is rendered uniform during the whole course of the experiment, by making the tube which conveys the air sufficiently long to reach nearly to the bottom of the vessel, as shown by the dotted line which passes down from the central opening at the top.

The quantity of carbonic acid in the air may be determined in the course of the same experiment. If the bulbs at *b* be filled with a strong solution of caustic potash (sp. gr. 1.25), and the tube *c*, with fragments of fused potash, the gain in weight which is experienced by the tubes *b*, and *c*, will indicate the quantity of carbonic acid which has been absorbed in the operation: the bent tube *d*, is filled with pumice-stone moistened with sulphuric acid; it is not weighed, but is merely interposed as a measure of precaution between the aspirator *e*, and the tube *c*, to prevent any accidental trace of moisture from passing backwards into *c*. The bulbs seen at *v*, are to be filled with potash to the extent shown in the enlarged drawing, fig. 232. This form of apparatus was contrived by Liebig. It is in continual requisition in the laboratory, for the purpose of absorbing gases which are transmitted through it; by placing it a little on one side, the gas is made to bubble up successively through each of the three lower bulbs, besides being brought thoroughly into contact with the liquid in the narrow portions of tubing which connect the different bulbs together. This simple contrivance has added greatly to precision in experiments of this kind.

FIG. 232.



The quantity of the other components of the atmosphere is materially diminished after long continued and heavy rains. Occasionally, from local and accidental circumstances, other gases and vapours are also met with. The average composition of the atmosphere in the climate of England, may however, be stated as follows, in 100 parts by volume.

• Oxygen . . . . .	20.61
Nitrogen . . . . .	77.95
Carbonic acid . . . . .	.04
Aqueous vapour . . . . .	1.40
• Nitric acid . . . . .	} traces
Ammonia . . . . .	
Carburetted hydrogen . . . . .	
and in towns. { Sulphuretted hydrogen . . . . .	} traces
• { Sulphurous acid . . . . .	

## CHAPTER III.

## WATER. HYDROGEN.

## § I. WATER.

*Symbol* (HO); *Equivalent* 9; *Combining Volume as Vapour*, 2;  
*Specific Gravity as Vapour* 0·622, *as Liquid*, 1·000.

(291) On the uses of water it is almost needless to enlarge, they are universally felt and appreciated. In each of its three physical conditions, the blessings it confers upon man are inestimable. As ice it furnishes in northern lands for months together, a solid bridge of communication between distant places: in the liquid condition, it is absolutely necessary to the existence of vegetable and animal life; in this shape, too, it furnishes to man a continual source of power in the flow of streams and rivers; it supplies one of the most convenient channels of communication between places widely separated; and further it is the storehouse of countless myriads of creatures fitted for use as food: in the state of vapour, as applied in the steam engine, it has furnished a power which has in later years done more than any other physical agent to advance civilization, to economize time, and to ameliorate the social condition of man. In each and all of these points if rightly considered, we must perceive the entire adaptation of this wonderful compound to the ends which it was designed by the Creator to fulfil.

It may further be observed that there is no form of matter which contributes so largely to the beauty and variety of the globe we inhabit. In its solid state we are familiar with it in the form of blocks of ice, of sleet and hail, of hoar frost fringing every shrub and blade of grass, or of snow protecting the tender plant as with a fleecy mantle, from the piercing frosts of winter. The rare but splendid spectacles of mock suns, or parhelia, are due to the refractive power of floating spiculæ of ice upon the sun's rays. In its liquid condition, as rain or dew, it bathes the soil: and the personal experience of all will testify to the charm which the waterfall, the rivulet, the lake, or the stream adds to the beauty of the landscape; whilst few can behold unmoved the unbounded expanse of ocean; which whether motionless, or heaving with the gently undulating tide, or when lashed into foam by the storm that sweeps over its surface, seems to remind man of his own insignificance, and of the power of Him who alone can lift up or quell its boiling waves. In

vapour how much variety is added to the view by the mist or the cloud; which by their ever-changing shadows diversify, at every movement, the landscape over which they are flitting; whilst the gorgeous hues of the clouds around the setting sun, and the glowing tints of the rainbow, are due to the refractive action of water and watery vapour upon the solar rays.

At the ordinary temperature of the air, when free from admixture, water is a clear, colourless, transparent liquid, destitute of taste or smell. At temperatures below  $32^{\circ}$  F. it freezes, and assumes a variety of crystalline forms derived from the rhombohedron and six-sided prism. Water evaporates at all temperatures, and under the ordinary pressure of the atmosphere it boils at about  $212^{\circ}$  F. Its anomalous expansion by heat (137), and the important purposes thereby attained (145), and the great dilatation which it undergoes on freezing (73), have been already pointed out. Arago and Fresnel have shown, that notwithstanding the gradual dilatation of water at temperatures below  $40^{\circ}$ , its refractive power on light continues regularly to increase as though it contracted. Its density at  $60^{\circ}$  F. is taken as 1.000, and it forms the standard with which, in this country, all solids and liquids are compared. A cubic inch of water at  $60^{\circ}$  F. weighs in air 252.456 grains.

To the chemist water is invaluable as a solvent. It is the perfection of a neutral substance; and it enters into combination most extensively both with acids and with bases. Experience has shown that when an acid has once been allowed to combine with water, the entire separation of the water from the acid is seldom practicable, unless some powerful base be presented to the acid; in such a case the base displaces the water, and its expulsion by heat is then easily effected. Suppose, for example, that sulphuric acid has been freely diluted with water; upon the application of heat the water at first passes off readily, leaving the less volatile acid behind. By degrees, however, it becomes necessary to increase the temperature in order to expel the water, and at last the acid begins to evaporate also, and finally no further separation can be effected, as, when the temperature rises to about  $620^{\circ}$  F. both water and acid distil over together. It is found on analysing the acid when it has reached this point, that the liquid contains one equivalent of acid and one of water ( $\text{HO}, \text{SO}_3$ ). But if to this concentrated acid an equivalent of potash, or one of oxide of lead, be added, the water is easily expelled, and an equivalent of anhydrous sulphate of potash ( $\text{KO}, \text{SO}_3$ ) or of sulphate of lead ( $\text{PbO}, \text{SO}_3$ ), is obtained. Water which supplies the place of a base in combination with acids, is called *basic* water.

In a similar manner water combines with the powerful bases, such as potash or soda, and then cannot be expelled from them until some acid has been added. Potash in the form in which it is obtained by evaporating down its aqueous solution and heating the residue to dull redness, consists of one equivalent of the alkali and one of water ( $\text{KO}, \text{HO}$ ), and this equivalent of water cannot be expelled except by the addition of an acid, such as sulphuric acid; then by the application of heat, anhydrous sulphate of potash is obtained as in the former instance. In this case the water in combination performs the part of an acid.

The compounds of water are frequently termed *hydrates*, and when a body is described as being entirely free from water in combination, it is commonly said to be *anhydrous*. Many salts in crystallizing unite with a definite quantity of water, which is essential to the form of the salt, but which may, by the application of a gentle heat, be expelled without altering the chemical properties of the saline body. In this case the water is spoken of as *water of crystallization*. Many salts part with such water by mere exposure to air. Carbonate of soda, for example, crumbles down, or *effloresces* to a white powder; and the same thing occurs in the case of sulphate of soda.\* The form of the salt depends upon the quantity of this water of crystallization. For instance, borax is always found to crystallize with 10 equivalents of water ( $\text{NaO}, 2 \text{BO}_3 + 10 \text{HO}$ ), in oblique rectangular prisms, if the solution of the salt be not sufficiently concentrated to begin to crystallize till the temperature falls to  $133^\circ \text{F.}$ ; but from a more concentrated solution borax is deposited in regular octohedra with only 5 equivalents of water. So, again, the sulphate of soda crystallizes in oblique four-sided prisms with 10 equivalents of water ( $\text{NaO}, \text{SO}_3 + 10 \text{HO}$ ) under ordinary circumstances, but if a solution, saturated at  $91^\circ$ , be very slowly raised to  $212^\circ$ , the sulphate of soda is deposited in rhombic octohedra which contain no water.

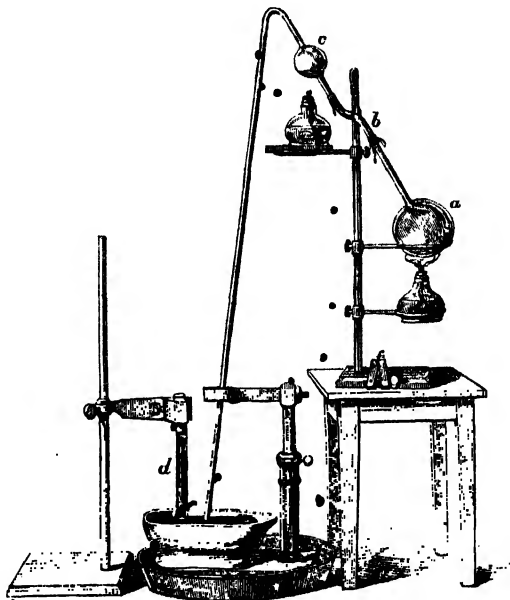
(292) *Various Kinds of Natural Waters*.—Owing to its extensive solvent powers, water is never met with naturally in a state of purity. *Rain water*, collected after a long continuance of wet weather, approaches nearest to it, but even that always contains

\* Other salts, on the contrary, absorb moisture from the atmosphere, and become damp or even liquefy in the water so absorbed; they are then said to *deliquesce*. Carbonate of potash, and chloride of calcium offer instances of this kind.

atmospheric air, and the gases floating in the air, to the extent of about  $2\frac{1}{2}$  cubic inches of air in 100 of water.\*

The quantity of air which is contained in spring or other water can be readily ascertained in the following manner. A globular flask, *a*, fig. 233, capable of containing 14 or 16 ounces, such as is used for taking the density of vapours, is filled with the water to be examined, and connected by a vulcanized caoutchouc tube, *b*, to a piece of barometer tube, upon which is blown a bulb, *c*, 2 inches or more in diameter. This tube is bent in the manner represented in the figure; the longer limb being upwards of 30 inches in length, and terminating below in a recurved extremity, which is intended to deliver the gas disengaged from the water, into a graduated jar, *d*, with an expanded funnel-shaped mouth, which is supported in a small mercurial bath. The bulb, *c*, having been about half filled with the water, is connected with the flask, by the caoutchouc tube,

FIG. 233.



which is firmly secured at both ends by ligatures. A small wooden vice, such as is seen at *f*, is made use of to compress the vulcanized tube and to cut off communication between the flask and the bulb, *c*. The water in *c* is now made to boil briskly for ten minutes or a quarter of an hour, until all the air is expelled from the tube, the mouth of which is kept just below the surface of the mercury. When, after a few minutes continued boiling, no more air escapes from the tube, the jar, *d*, is filled with mercury, and placed over the end of the long tube. The vice is removed, and heat applied to the flask; the water speedily begins to give off gas; and the quantity increases till the water boils. The ebullition must be continued steadily for a full hour, and the operation terminated by a few minutes brisk boiling, by which the delivery tube will be filled with steam, and all the air will be driven over into the jar. The object of the globe, *c*, is to prevent the water from boiling over into the jar. A little steam always condenses in the air jar above the mercury, but this is a matter of small consequence. When the operation has terminated, the gas is allowed to cool, and is transferred to a tall jar of water, or of mercury, where its bulk can be measured.

It will be found that all water, including even that which has been recently distilled, contains air. For example, three samples of water twice distilled in glass vessels, were submitted to experiment: 100 cub. in. of the first specimen contained 1.85 cub. in. of air; in the same bulk of the second 2.15, and the third specimen 2.38 cub. in. of air were present; the oxygen and nitrogen being in each case almost exactly in the proportion of 1 measure of oxygen, to 2 of nitrogen.



*Spring Water*, although it may be perfectly transparent, always contains more or less of saline matter dissolved in it; the nature of these salts will of course vary with the character of the soil through which the water percolates. The most usual saline impurities, are carbonate of lime, common salt, sulphate of lime, and sulphate and carbonate of magnesia. The waters of the New Red Sandstone are impregnated to a greater or less extent with sulphate of lime. Most spring waters are charged with a notable proportion of carbonic acid, which dissolves a considerable amount of carbonate of lime; the calcareous springs in the chalk districts around London contain from 18 to 20 grains of chalk per gallon, 6 or 8 grains of which separates by exposure of the water to the atmosphere, so that a running stream will seldom contain more than 12 or 14 grains of chalk per gallon in solution. Waters which have filtered through a bed of chalk also often contain carbonate of soda in considerable quantity, as is the case with the deep-well waters of London.

*Mineral Waters* are waters impregnated with a large proportion of any one of the above-named salts, or with some substance not so commonly met with; such waters are usually reputed to possess some medicinal quality, varying with the nature of the salt in solution. Many of these springs are of a temperature considerably higher than that of the surface of the earth where they make their appearance. At Carlsbad and Aix-la-Chapelle this temperature varies from  $160^{\circ}$  to  $190^{\circ}$ . Such hot springs either occur in the vicinity of volcanoes, and then generally abound in carbonic acid, common salt, and other salts of soda; or they spring from great depths in the rocks of the earliest geological periods, and contain chlorides of calcium and magnesium, and almost always traces of sulphuretted hydrogen. (Berzelius.)

Many mineral waters contain oxide of iron, which imparts to them an inky taste; they are then frequently termed *chalybeate* waters: some of the Cheltenham springs are of this kind. In other instances carbonic acid is very abundant, giving the brisk *effervescent* character noticed in Seltzer water. Less frequently, as in the Harrogate water, sulphuretted hydrogen is the predominating ingredient, giving the nauseous taste and smell to such *sulphureous* waters. In other instances the springs are merely *saline* and contain purgative salts, like the springs at Epsom, which abound in sulphate of magnesia, and at Cheltenham, where common salt and sulphate of soda are the predominant constituents. Many of these saline springs also contain small quantities of iodine and bromine, which greatly add to their therapeutic activity.

*River Water* is less fitted for drinking than ordinary spring water, although it often contains a smaller amount of salts; it usually holds in solution a much larger proportion of organic matter of vegetable origin, derived from the extensive surface of country which has been drained by the stream. If the sewerage of large towns situated on the banks be allowed to pass into the stream, it is of course still less fit for domestic use. Running water is, however, endowed with a self-purifying power of the highest importance; the continual exposure of fresh surfaces to the action of the atmosphere promotes the oxidation of the organic matter, and if the stream be unpolluted by the influx of the sewerage of a large town, this process is generally fully adequate to preserve it in a wholesome state. River water almost always requires filtration through sand before it is fit for domestic use; and if water works designed to supply such water be properly constructed, provision is made for such a filtration. Suspended matters, such as weeds, fish-spawn, leaves, and finely divided silt or mud, are thus removed; but vegetable colouring matter in solution, salts, and other bodies, when once they are dissolved cannot be arrested by the filter.

Water is familiarly spoken of as *hard* or *soft*, according to its action on soap. Those waters which contain compounds of lime or magnesia occasion a *curdling* of the soap, as these earths produce with the fat of the soap a substance not soluble in water. Soft waters do not contain these earths, and dissolve the soap without difficulty. Many hard waters become softer by boiling; in which case the carbonic acid is expelled, and the carbonate and part of the sulphate of lime which were held in solution are deposited, and cause a fur or incrustation upon the inside of the boiler.

*Sea Water* is largely impregnated with common salt, and with chloride of magnesium, to which it owes its saline bitter taste. The quantity of salts is continually on the increase, as it is the receptacle for all the fixed contents of the river water which is discharged into the ocean, since pure water alone evaporates from its surface. The specific gravity of sea water is subject to trifling variations, according to the part of the globe from which it is taken. The waters of the Baltic and of the Black Sea are less salt than the average, while those of the Mediterranean are more so. The waters of the Mediterranean in the Levant are more salt than those of the same sea near the Straits of Gibraltar. The mean specific gravity of sea water is 1.027, and the quantity of salts ranges from 3.5 to 4 per cent. According to M. Schweitzer (*Phil. Mag.*, 1839, vol. x., p. 58), the water of the British Channel is composed as

follows :—that of the Mediterranean, analysed by M. Usiglio (*Ann. de Chimie*, III., xvii., 104) will be seen to agree very closely with it in composition :—

	British Channel.	Mediterranean.
Water . . . . .	964.74372	962.345
Chloride of sodium . . . . .	27.05948	29.424
Chloride of potassium . . . . .	0.70552	0.505
Chloride of magnesium . . . . .	3.66658	3.219
Bromide of magnesium . . . . .	0.02929	0.556
Sulphate of magnesia . . . . .	2.29578	2.477
Sulphate of lime . . . . .	1.40662	1.357
Carbonate of lime . . . . .	0.03301	0.114
Iodine . . . . .	traces	.
Ammonia . . . . .	traces	.
Oxide of iron . . . . .	...	0.003
	<hr/> 1000.00000	<hr/> 1000.000

Specific gravity . . . . . 1027.4 at 60° F. 1025.8 at 70° F.

Minute quantities of iron have been found in the waters of the ocean, but nitric and phosphoric acids have eluded the most careful observation.

For chemical purposes water is always purified by distillation, which may be effected on a small scale in glass retorts, but it is generally carried on in a copper still provided with a pewter or copper worm. Iron pipes may also be safely used for the purpose of condensation; but lead must be avoided. The still should not be employed for any other purpose. When a few drops of distilled water are evaporated upon a slip of glass, no stain or mark should be left, otherwise some saline impurity is present.

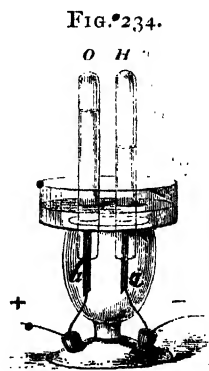
Water was long supposed to be an elementary substance. This, however, is not the case: it is a compound of oxygen with hydrogen, in the proportion of 1 equivalent of each; its symbol is therefore HO, and its combining number 9. When converted into vapour, 9 grains of steam occupy twice the bulk of 8 grains (or 1 equivalent) of oxygen at the same temperature; its combining volume is therefore = 2; the combining volume of oxygen being taken as 1.

## § II. HYDROGEN.

*Symbol* (H); *Equivalent*, 1; *Specific Gravity*, 0.0692; *Combining Volume*, 2.

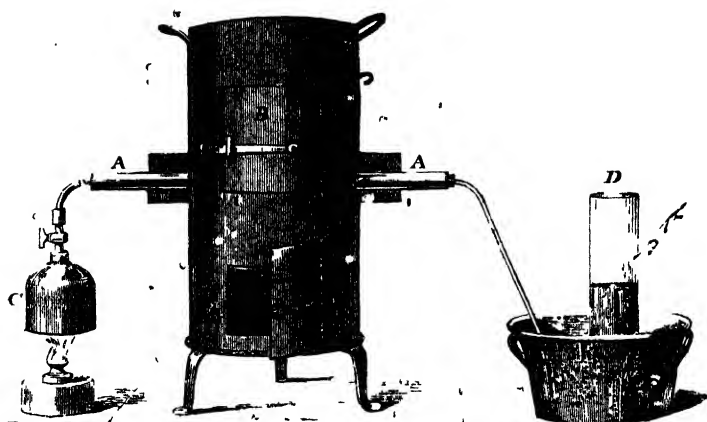
(293) *Preparation*.—The composition of water may be determined both by analysis or separation of its constituents, and by synthesis or their reunion after such separation. An elegant mode of showing the composition of water analytically, is afforded by

the voltaic battery. A glass vessel, fig. 234, containing two platinum plates, *a* and *b*, is filled with water, slightly acidulated with sulphuric acid to improve its conducting power, and is arranged so as to transmit the current of a battery consisting of three or four pairs of Grove's cells (233). Immediately that the two platinum plates are connected with the wires of the battery, gas rises from each; and if two similar jars be filled with water and inverted one over each plate, the volume of the gas which rises from the platinum, or negative plate, *b*, will be found exactly double of that which rises from the zinc, or positive plate, *a*: the gas in *a* will show itself to be oxygen by rekindling a glowing match, whilst that in *b* extinguishes flame, but takes fire itself when a light approaches it. To this gas the name of *hydrogen*, or 'producer of water,' has been given. Oxygen and hydrogen are the sole constituents of water, and by their union in the proportion of two measures of hydrogen to one of oxygen this liquid is reproduced.



The presence of hydrogen and oxygen in water may be shown in other ways, and hydrogen may be obtained by chemical means. If a piece of potassium the size of a pea be wrapped up in blotting paper, and be rapidly introduced beneath the mouth of a strong wide tube, 10 or 12 inches long, filled with water and inverted in the pneumatic trough, bubbles of gas will be quickly disengaged, and will collect in the upper part of the tube. On inverting the tube and applying a light, the gas will take fire and burn with flame; the liquid in the tube will be found to be alkaline, and will change the yellow colour of turmeric to brown; potash having been formed by the combination of the potassium with oxygen derived from the water. Hydrogen may be also obtained by the action of water upon iron at a high temperature. In order to effect this, let a piece of iron piping, shown at *A A*, fig. 235, be filled with iron turnings, and heated to redness in a portable furnace, *B*; and let a current of steam be driven through the tube from a small boiler, *C*, attached to one extremity of the pipe: the aqueous vapour in its passage will be decomposed, the oxygen will enter into combination with the heated iron, whilst the liberated hydrogen will pass on, and may be collected over water in a jar, *D*, placed over the mouth of a bent tube attached to the other extremity of the iron pipe.

FIG. 235.



But the most convenient way of procuring hydrogen is by the action of diluted sulphuric acid on zinc. The zinc may be melted in an iron ladle, and poured from the height of a few feet into a pail of cold water, by which means it is *granulated*, or reduced into grains or flakes: about half an ounce of the granulated zinc is introduced into a retort, and a dilute acid, prepared by mixing an ounce of oil of vitriol cautiously with 6 ounces of cold water, stirring all the while, is poured upon the zinc. Hydrogen gas is soon evolved in great abundance: the first portions of gas which are contaminated with the air contained in the retort, must be allowed to escape; afterwards the gas may be collected in the usual way. In this process the zinc takes oxygen from the water, and forms oxide of zinc, which, though insoluble in water, is immediately dissolved by the sulphuric acid, forming a salt called sulphate of zinc, while the hydrogen passes off in the gaseous form. The change may be illustrated by the following diagram:—

*Decomposition of Water by Zinc and Sulphuric Acid.*

Before decomposition.

9 = 1 eq. to { 1 = 1 eq. Hydrogen (H)  
 water (H<sub>2</sub>O.) { 8 = 1 eq. Oxygen (O)  
 32 = 1 eq. Zinc (Zn) ————  
 40 = 1 eq. Sulphuric acid, (SO<sub>3</sub>)

After decomposition.

liberated.  
 { 1 eq. sulphate  
 80 of oxide of zinc  
 (ZnO, SO<sub>3</sub>).

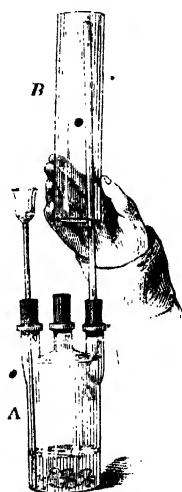
Or in symbols;  $\text{Zn} + \text{H}_2\text{O}, \text{SO}_3$  give  $\text{H}_2 + \text{ZnO}, \text{SO}_3$ .

An ounce of zinc is sufficient to liberate from water about  $2\frac{1}{2}$

gallons of the gas. Scraps of iron may be substituted for zinc; but in this case the gas is less pure. The gas furnished by the action of dilute sulphuric acid on zinc possesses a peculiar odour, and is frequently contaminated with small quantities of compounds of hydrogen with sulphur, arsenic, and carbon. It may be freed from these impurities by causing it to pass first through a strong solution of potash, and then through a solution of corrosive sublimate, or of nitrate of silver.

*Properties.*—Hydrogen is an elementary substance, and when obtained with the precautions just mentioned, is a colourless, transparent, tasteless, and inodorous gas. It has never been liquefied, and is even less soluble in water than nitrogen. Hydrogen is the lightest form of matter which is known; it is only  $\frac{1}{16}$ th of the weight of an equal bulk of oxygen, and little more than  $\frac{1}{15}$ th of that of air. Its specific gravity is 0.0692, and 100 cubic inches weigh but 2.14 grains. Owing to its levity, it has been extensively used for aerostatic purposes, although the facility with which coal gas can now be obtained has caused this latter, notwithstanding its much greater density, to be universally substituted for hydrogen in filling balloons. A light bag made of the craw of a turkey may easily be inflated with hydrogen, and will ascend rapidly, and carry with it a weight of several grains. Owing to its lightness, a jar may be easily filled with the gas by *displacement* without using the pneumatic trough. A tube 8 or 10 inches long, is fixed by a cork in a three-necked bottle in the manner shown at A, fig. 236, containing some granulated zinc; acid is introduced through the funnel, and the gas, after the atmospheric air in the bottle has been allowed to escape, may be collected by holding a jar over the tube, as at B. The hydrogen will be retained for some minutes even if the jar be removed, and be still held in the inverted position; while if the mouth be turned upwards, the gas will have escaped after the lapse of a few seconds. Hydrogen has a smaller equivalent number than any other elementary body, and it has hence been taken as the unit or standard of comparison. Its equivalent number is therefore unity, or, 1, and its combining volume 2, or double that of oxygen: the combining volume of a gas being the proportion in bulk in which it enters into com-

FIG. 236.



bination with other gases, as compared with the bulk occupied by an equivalent quantity of oxygen, under similar circumstances of temperature and pressure. Pure hydrogen, though it cannot support life, is not poisonous, and when mixed with a certain proportion of oxygen it has been breathed for some time without inconvenience; but, owing to its rarity, it renders the voice temporarily much sharper and more shrill than usual.

(294) *Synthesis of Water—Eudiometers.*—Hydrogen is extremely inflammable; when a lighted taper is plunged into a jar of it the gas takes fire, but the taper is extinguished. A jet of hydrogen burns with a pale yellowish, feebly luminous flame, but gives out great heat. If the gas be dried by causing it to pass through a tube containing chloride of calcium, and a cold bell jar be held over the burning jet, the interior of the glass quickly becomes bedewed with moisture, owing to the formation of water by the union of the burning hydrogen with the oxygen of the atmosphere.

FIG. 237.

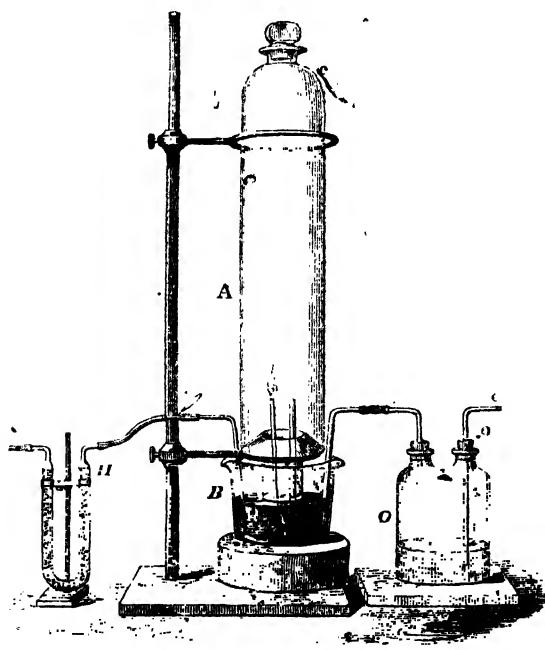


Fig. 237 exhibits an apparatus in which a jet of hydrogen is shown burning in an atmosphere of oxygen: the hydrogen is dried as it passes through the bent tube, H, which is filled with fragments of chloride of calcium. The jar, A, which is open at its lower end, is filled by displacement with dry oxygen; the jet of hydrogen is kindled, and then the jar is quickly depressed over the burning gas, into the mercury con-

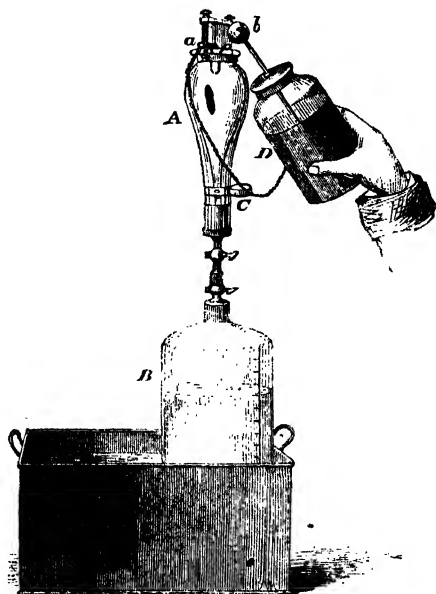
tained in the vessel, B. As the oxygen is consumed a fresh supply is maintained through the tube connected with the bottle, O, which contains concentrated sulphuric acid for the purpose of depriving the oxygen of the small quantity of moisture which it would otherwise

carry into the jar, A. The oxygen and hydrogen are supplied from separate gas-holders, not shown in the figure. The water condenses on the sides of the jar, and collects in the gutter at the lower part. Oxygen and hydrogen may be kept in a state of mixture at the ordinary temperature of the air for an unlimited period without entering into combination; but the passage of an electric spark, the application of a lighted or even of a glowing match, and, in some instances, the mere contact of a cold metallic substance, such as platinum, especially if in a finely divided state (62), is sufficient to determine their immediate combination. Sudden compression of the gases, when mixed, produces the same effect from the heat evolved, whilst a still greater amount of compression, if it be gradually applied, even when carried to 150 atmospheres, fails to produce their union.

Cavendish, in his inquiries respecting the formation of water, effected the combination of the two gases by means of the electric spark. He employed for this purpose a strong glass vessel, a modification of which is represented at A, fig. 238.

Through the upper part two platinum wires are inserted to within the eighth of an inch of each other. The vessel can be closed at the bottom by a glass stopcock, c. The air is exhausted, and the vessel screwed upon the top of a jar, B, containing a mixture of two measures of hydrogen and one of oxygen: on opening the stopcocks a portion of the mixture enters the vessel; the cocks are then closed, and an electric spark passed through the mixture by discharging a small

FIG. 238.



electric spark passed through the mixture by discharging a small Leyden jar, D, through the platinum wires, a, b. A bright flash is seen at the moment of the discharge, and the gases combine, forming steam, which condenses on the sides of the glass; the whole of the two gases, if mixed in the above proportions, enter



into combination with each other. On again opening the stopcocks a fresh quantity of the gases may be admitted, to supply the place of those just condensed, the spark may again be transmitted, and the process may be repeated till the whole of the gases are consumed, and a considerable quantity of water formed.

The uniformity of composition and regularity of proportion in which compounds are produced when they combine chemically is strikingly illustrated by means of a mixture of oxygen and hydrogen gases. The two gases may be mixed in any arbitrary proportion in a suitable vessel, into the sides of which two platinum wires are fused for the purpose of transmitting the electric spark. If the mixture be capable of exploding at all, the combination will be found to have occurred in the proportion of two measures of hydrogen to one of oxygen, no matter in what proportion the gases were mingled. If oxygen be used in excess, the superfluous oxygen will be found remaining uncombined, and if hydrogen be in excess, this excess will remain uncombined.

Upon this principle a valuable instrument, the *Eudiometer*, is constructed, by means of which various gaseous mixtures may be analysed with great exactness. Many different forms of this instrument are in use. One of the simplest and most convenient is that proposed by Dr. Ure. It consists of a stout siphon tube,

FIG. 239.

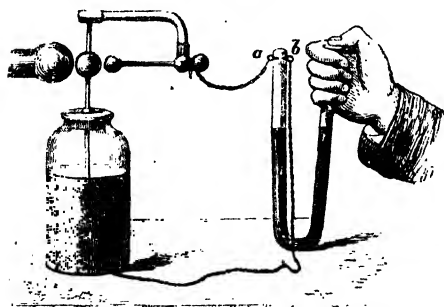


fig. 239, open at one extremity and closed at the other. Into the sides of the tube, near the sealed end, two platinum wires, *a b*, are fused, for the purpose of transmitting an electric spark through the cavity of the tube. The sealed limb is accurately graduated to hundredths of a cubic inch, or other suitable divisions.

Suppose it be desired to ascertain the proportion of oxygen in atmospheric air, the instrument is first filled with mercury, and then a small quantity of air is introduced: the bulk of this air is accurately measured, taking care that the liquid stands at the same level in both tubes. A quantity of pure hydrogen about equal in bulk to the air is next introduced, and the bulk of the mixture is accurately measured. The open extremity of the tube is now closed with the finger,

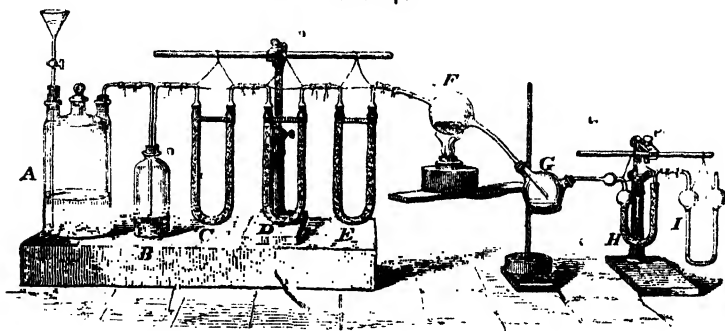
below which a column of atmospheric air is safely included; this portion of air acts as a spring which gradually checks the explosive force, when the combination is effected by passing a spark across the tube by means of the platinum wires. The bulk of the gas, after the explosion, diminishes, owing to the condensation of the steam which has been formed. Mercury is therefore again poured into the open limb, until it stands at the same level in both tubes, and the volume of the gas is measured a third time. One third of the gas that has been condensed by the explosion will represent the entire quantity of oxygen which the mixture contained. For delicate experiments, a very complete though expensive form of eudiometer has been contrived by Regnault.

If a mixture of oxygen and hydrogen be fired in the air in considerable quantity, as when a bladder full is ignited, or still better, when a little soapsuds are blown up into a lather by forcing some of the gaseous mixture out of a bladder through a pipe under the liquid, a loud and sharp report attends the combination, the steam formed suddenly expands from the high temperature attendant on the combustion, and immediately afterwards condenses: great dilatation is first produced, followed by the formation of a partial vacuum; the surrounding air rushes in to fill the void, and by the collision of its particles produces the report. If the hydrogen be mixed with air, a similar but feebler explosion occurs when a light is applied; hence it is especially necessary in all experiments with hydrogen to allow time for the expulsion of the atmospheric air from the apparatus before setting fire to the issuing jet. The explosion is most violent when 2 measures of hydrogen are mixed with 5 of air: if the mixture be diluted with a large excess either of hydrogen or of air, the explosion becomes more feeble; the heat evolved is less intense, and the combustion less sudden, until at a certain degree of dilution no explosion follows the application of flame, the mixture burns slowly, or if still more diluted, it takes fire only just at the spot where the heat is applied, but the combustion does not spread through the mass.

If a long tube, open at both ends, be held over a jet of burning hydrogen, a rapid current is produced through the tube which occasions a flickering in the flame, attended by a series of small explosions that succeed each other so rapidly and at such regular intervals as to give rise to a musical note, the pitch and quality of which varies with the length, thickness, and diameter of the tube.

Pure water may be formed in considerable quantities, by a method different from those hitherto described; the operation at the same time furnishes a means of accurately ascertaining the relative weights of oxygen and hydrogen which enter into the composition of water. It consists in passing a current of hydrogen over a weighed quantity of oxide of copper: at a red heat hydrogen deprives the oxide of copper of its oxygen and forms water; and by determining the weight of the water thus produced, and the loss sustained by the oxide of copper, the proportion of hydrogen which has combined with the oxygen can be ascertained. The apparatus

FIG. 240.



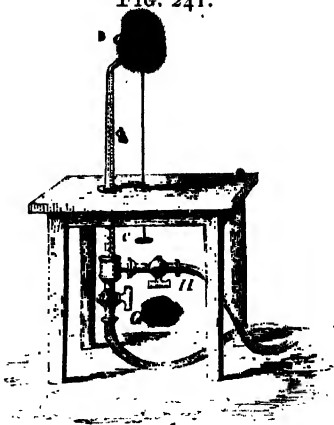
required for the purpose is represented in fig. 240. A quantity of oxide of copper is placed in the globe, *F*, which is constructed of glass of difficult fusibility, and the globe and its contents are accurately weighed. A current of hydrogen, prepared from zinc and sulphuric acid in the bottle, *A*, is allowed to bubble up through a solution of potash, *B*, and to traverse three bent tubes in succession; the first, *C*, is filled with fragments of pumice-stone moistened with a solution of corrosive sublimate ( $\text{Hg Cl}$ ); the second, *D*, contains fragments of fused caustic potash; and the third, *E*, is charged with pumice moistened with oil of vitriol. The mercurial salt and the potash remove the traces of arsenic, sulphur, and carburetted compounds, which the gas might otherwise carry over, and the oil of vitriol absorbs the last traces of moisture. Perfectly pure and dry hydrogen gas is thus delivered in the globe, *F*. When all the air is completely displaced, heat is applied to the globe; the oxide of copper gives up its oxygen; water is formed, which condenses in the receiver, *G*, and in the attached bent tube, *H*, which is filled with fragments of pumice moistened with oil of vitriol: the whole of the water formed is by this means arrested. *I* is a bulb

tube containing a little oil of vitriol, which prevents the entrance of extraneous moisture, and by its motion shows the progress of the gas. On weighing the globe, *r*, with the oxide after the experiment has terminated, the loss gives the quantity of oxygen which has combined with the hydrogen; whilst the difference between the amount of oxygen and that of the water condensed in the receiver, *g*, and tube of acid, *h*, shows the quantity of hydrogen that has combined with it. Each grain of hydrogen is in this manner proved to require exactly 8 grains of oxygen for its conversion into water.

Many other metallic oxides besides oxide of copper, when heated in a current of hydrogen, part with their oxygen, and are brought back to the metallic condition. If the bulb be weighed first when empty, then when charged with oxide, and a third time after the stream of gas has been continued till all formation of water ceases, and till the tube has become cool, the loss of weight sustained by the oxide furnishes the proportion of oxygen combined with the metal. A true and very accurate analysis of the oxide will thus have been effected: 40 parts of oxide of copper are found in this way to contain 32 of copper and 8 of oxygen.

Hydrogen in the act of combining with oxygen, emits a very intense heat. By throwing a jet of oxygen into a flame of coal-gas or of hydrogen, or still better by introducing a jet of oxygen, as at *o*, fig. 241, into the centre of a jet connected at *h* with a gas-holder supplying hydrogen, so that the two gases may be mixed just before they issue from the common orifice of the tube *a*, a heat may be obtained which can scarcely be surpassed. Sometimes the two gases are mixed in the proportion of 2 volumes of hydrogen to 1 of oxygen, and introduced into a bladder and burned as they issue through a tube of particular construction, contrived by Mr. Hemming. This safety jet consists of a brass tube, about 6 inches long and two-thirds of an inch in diameter, filled with pieces of very fine brass wire, which are packed closely together, and then wedged in very tightly by driving a stout conical piece of wire into the axis of the tube (402). This tube is supplied at one extremity with a blowpipe jet, and at the other with a screw

FIG. 241.



which can be connected with a stopcock adjusted to the neck of the bladder. The temperature produced by burning the mixed gases from such a jet is so intense that thick platinum wire melts in it with ease, and is partially volatilized; iron and steel melt and burn with vivid scintillations. Rock crystal may be liquefied, and drawn out into threads like glass, and the stem of a tobacco pipe may be fused into an enamel-like bead. When the oxyhydrogen flame, which is but very feebly luminous, is directed upon a small cylinder of lime, *b*, this earth does not fuse, but it becomes white hot, and then emits a very pure white light of great steadiness and intensity, which may be maintained for hours if care be taken to expose to the flame fresh surfaces of the lime by causing it to revolve by clockwork, continually but very slowly. This object may be obtained less perfectly by occasionally turning the pin, *c*, which supports the lime. Without this precaution a cavity would be formed opposite to the jet from volatilization of a small quantity of the lime. This light was originally proposed by Lieutenant Drummond, to be used in the trigonometrical survey of Great Britain, and it is astonishing at what distances it may be seen when the rays are concentrated by a parabolic reflector. On the 31st December, 1845, it was seen across the Irish Channel, at half-past 3 P.M. (during daylight) from the top of Slieve Donard, in Ireland, by an observer stationed at the top of Snowdon,—an interval of 108 miles in a direct line; and it has more than once been seen at a distance of 112 miles.

A striking experiment may be performed with hydrogen, which shows how purely conventional are the terms 'combustibles' and 'supporters of combustion.' Let a tall bottle with a narrow neck be filled with hydrogen gas; through a cork which passes easily into the neck of the bottle fit a jet connected with a gas-holder containing oxygen; place the bottle mouth downwards and set fire to the hydrogen, then immediately insert the cork and jet, through which a stream of oxygen is gently issuing. The flame will appear to attach itself to the oxygen tube, and the jet of oxygen will be burning in an atmosphere of hydrogen. Combustion, in fact, occurs at the place where the two gases first come into contact. Suppose, for a moment, that the earth's atmosphere had contained hydrogen instead of oxygen; oxygen would have appeared to us in the light of a combustible gas, and hydrogen in that of a supporter of combustion.

## CHAPTER IV.

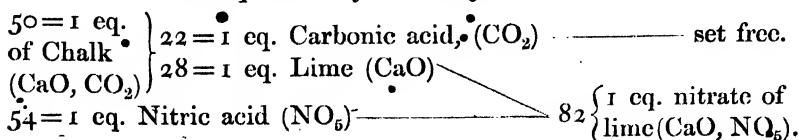
## CARBON. CARBONIC ACID.

§ I. CARBONIC ACID, ( $\text{CO}_2$ ); *Equivalent*, 22; *Combining Volume*, 2; *Specific Gravity*, 1.529.

(295) An atmosphere composed only of oxygen, nitrogen, and steam, though perfectly adapted to the support of animal life, would be unfit to sustain vegetation. Plants require for their growth and development a certain proportion of another gas—carbonic acid. Evidence of the existence of this body in the air is easily obtained by exposing a saucer of lime water to the atmosphere; in a few minutes its surface becomes covered with a thin pellicle, which if disturbed by agitation sinks to the bottom. The pellicle is renewed after each agitation until the whole of the lime contained in the liquid has been thus rendered insoluble. This white matter is chalk, which is a compound of carbonic acid and lime. Such compounds of carbonic acid with bases are termed *carbonates*, hence chalk is chemically termed *carbonate of lime*. When the chalk thus obtained is heated to bright redness (which, if the result is to be accurately examined, must be effected in a platinum tube), carbonic acid is expelled, as a colourless and transparent gas, while pure quick lime is left behind.

*Preparation.*—In actual practice carbonic acid is obtained by a much more convenient plan. Carbonic acid being but a feeble acid, is expelled from its compounds by almost every other acid which dissolves freely in water; it is therefore easily separated from its compounds by the addition of one of these acids. Fragments of chalk, or of marble, which is a more compact form of carbonate of lime, are placed in a retort or gas-bottle, and some powerful acid, such as the nitric or the hydrochloric, diluted with 8 or 10 times its bulk of water, is poured upon the chalk, when the acid seizes the lime and displaces the carbonic acid, which escapes with a violent effervescence. The following diagram shows the nature of this decomposition when chalk and nitric acid are employed:—

*Decomposition of Chalk by Nitric Acid.*



Or in symbols;  $\text{CaO}, \text{CO}_2 + \text{NO}_5 \text{ give } \text{CaO}, \text{NO}_5 + \text{CO}_2$ .

Limestone, Iceland spar, peatlash, and carbonate of soda, all yield carbonic acid when acted on by a stronger acid.

*Properties.*—Under atmospheric temperatures carbonic acid is a colourless transparent gas, with a faint acidulous smell and taste; when generated in a confined space in strong vessels, it however condenses to a liquid as transparent and colourless as water. At  $32^{\circ}$  F. it requires a pressure of 38.5 atmospheres to retain it in the liquid state (Faraday). It then has a specific gravity of 0.83, whilst at  $86^{\circ}$  F. the specific gravity is only 0.60 (Thilorier, *Ann. de Chimie*, II., lx., 427). By the application of heat it expands four times more rapidly than air; its expansion much exceeds that of any known substance, liquid or gaseous. Liquefied carbonic acid does not mix freely with water, or with the fixed oils; but it is dissolved by alcohol, ether, oil of turpentine, naphtha, and bisulphide of carbon in all proportions. When a stream of the liquefied acid is allowed to escape into the air, it freezes into a snow-white solid (182); and if a tube containing liquid carbonic acid be plunged into a bath of the solid acid mixed with ether, and placed in the vacuum of the air pump, the liquid carbonic acid in the tube will speedily be frozen into a clear transparent ice-like mass, which melts at  $-70^{\circ}$  F. The solidified acid is heavier than the liquid portion in which it is forming.

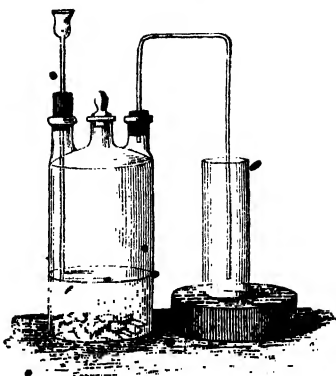
Carbonic acid gas is not inflammable, neither will it support the flame of burning bodies; the extinction of a taper is one of the means frequently resorted to for detecting its presence. Many other gases, however, have the same property; some additional test, therefore, becomes necessary. Such a test is afforded by its action upon lime-water, which, when agitated with the gas, is immediately rendered milky from the formation of chalk; a few drops of any strong acid dissolve the chalk and restore transparency to the liquid; an excess even of carbonic acid has the same effect.

Carbonic acid gas in its concentrated form is irrespirable; for by producing spasm of the glottis it is prevented from entering the lungs; when diluted with air, however, it may be breathed without even a suspicion of its presence. If the proportion exceed 3 or 4 per cent. of the air it acts as a narcotic poison; and even in much smaller quantities its depressing effects are very injurious. The ill effects experienced in crowded and ill-ventilated rooms are chiefly due to the presence of this gas in undue quantity, and it is this circumstance which renders attention to ventilation a matter of such high importance.

Carbonic acid gas is more than half as heavy again as atmospheric air; 100 cubic inches of it at  $60^{\circ}$  F. and 30 inches Bar.

weigh 47.303 grains, and its specific gravity is 1.529. From its density it may easily be collected in dry vessels by displacement, as represented in fig. 242, and may be poured from one vessel into another like water.

FIG. 242.



Carbonic acid gas dissolves in water to a larger extent than any of the gases as yet described. At the ordinary temperature water takes up about two-thirds of its bulk of carbonic acid, and its solubility increases if the pressure be increased. When the compression is suddenly removed, the gas escapes with brisk effervescence. Advantage is taken of this circumstance in the preparation of *soda-water*, as it is called. For this purpose the water, which may or may not contain soda or other substances in solution, is mechanically charged with a large quantity of carbonic acid gas, by the use of a condensing syringe, attached to a reservoir filled with the gas. The excess of the gas thus forced into the liquid occasions the agreeable briskness and pungency so much prized in this beverage. A solution of carbonic acid in water produces a feeble and fugitive reddening of litmus paper. This solution possesses solvent powers which, though in many instances extremely feeble, are yet far more extensive than those of pure water. By the continuous action of water charged with carbonic acid, even granite and the hardest rocks are disintegrated, few finely divided minerals being able to resist its gradual and long continued action. The proportion of gas dissolved is in many instances very minute, but as few natural sources of water exist which are not to a greater or less extent impregnated with carbonic acid, either by absorption from the atmosphere or from the soil, the solution, insignificant as it may at first sight appear, is continually proceeding, and in the lapse of time it effects changes of great importance and extent.

The briskness of spring water is partly due to the carbonic acid which it contains; though its usual coolness and the abundance of atmospheric air dissolved in it, are still more important. It is the absence of these qualities which renders boiled or distilled water flat and insipid. Carbonic acid was originally termed *fixed air*, from the circumstance of its having been discovered by Dr. Black, in 1757, as a solid or fixed constituent in limestone, and



from its becoming fixed or absorbed by solutions of the pure alkalies.

(255) *Sources of Carbonic Acid*.—Besides the processes of procuring the gas already described, there are a variety of cases in which it is produced on a very large scale in nature. Respiration in animals is always attended with the formation of a large proportion of the gas. This fact may be easily proved by forcing air from the lungs by means of a tube through lime-water, which will speedily become milky from the deposition of carbonate of lime. The proportion of carbonic acid in respired air varies from 3 to 4 per cent., being usually about  $3\frac{1}{2}$  per cent. Carbonic acid is also abundantly disengaged in the process of fermentation, and is the cause of the briskness of bottled beer, champagne, and other fermenting liquors. Many accidents have occurred from persons incautiously descending into an empty fermenting vat before the gas has had time to escape and mix with the air; it is usual to facilitate the escape of the dense gas by leaving the plug at the bottom of the vessel open for some hours. In the operation of burning lime in the lime-kiln, the heat expels from the limestone the carbonic acid, which escapes in large volumes. Many a poor houseless wanderer, tempted by the warmth of the kiln, has lain down in the stream of air proceeding from it, and has slept to wake no more. By the operation of subterranean heat in volcanic districts upon limestone beneath the surface, large volumes of carbonic acid are continually finding their way into the atmosphere; immense quantities are discharged from open craters or from fissures and cavities in the soil; the springs in such districts are also frequently highly charged with it, and the gas escapes with effervescence when they reach the surface. The springs of Seltzer, Pyrmont, and Marienbad, on the Continent, and of Tunbridge, in our own country, exhibit this phenomenon.

The carbonic acid met with in spring water is in many instances derived from the gradual oxidation of the vegetable and other organic matter which it holds in solution, by the action of the oxygen of the air which all waters naturally contain. The lake waters from the primitive districts, such as those in the northern parts of Scotland, leave scarcely any residue on evaporation except a little organic matter; they are very free from carbonic acid, and the proportion of oxygen is somewhat more than one half that of the nitrogen. If such waters be kept in closed vessels for a few weeks in a warm room, the oxygen gradually decreases, and in its place a corresponding volume of carbonic acid is found. Spring waters which rise in a sandy district, the surface of which is

sparingly clothed with vegetation, and from which consequently they can take up but little organic matter, contain but small quantities, often, mere traces, of carbonic acid; whilst the springs of highly cultivated districts, such as those which rest more or less directly upon the chalk, become charged with organic matter, which gradually undergoes oxidation in the soil, and the quantity of carbonic acid contained in such waters is always considerable, whilst the quantity of oxygen is proportionately reduced. In some experiments made upon this subject, the water of the Thames, for example, was found to contain about 5.5 cubic inches of carbonic acid per gallon; that of the New River, 4.84; and that of the deep chalk well in Trafalgar-square, 7.2 cubic inches; whilst the pure water of Loch Katrine did not contain 0.06 cubic inches when first collected, though after it had been kept for a few weeks in a warm room in a closed bottle, the quantity of carbonic acid in the same sample, owing to the gradual oxidation of the organic matter in solution, had increased to 0.38 cubic inches in the gallon, whilst the oxygen had diminished to a similar extent.\*

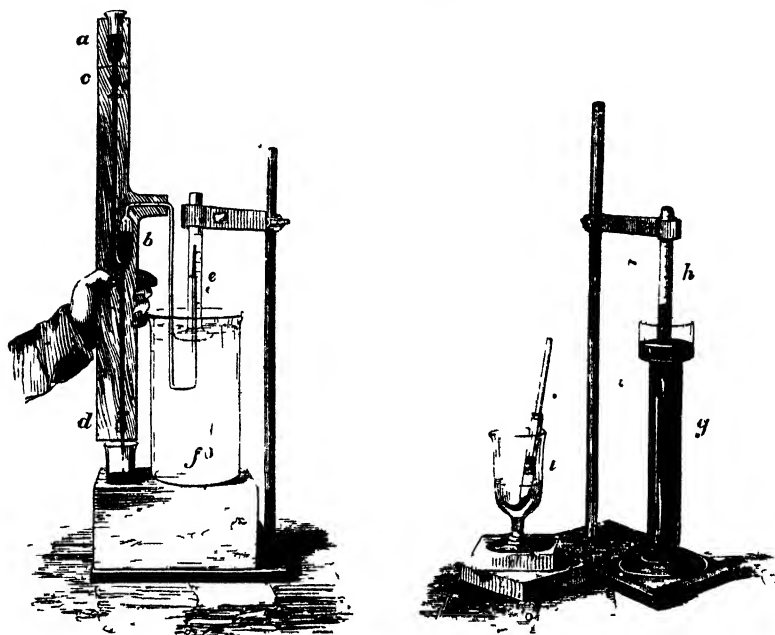
The analysis of these gases, or of any mixture of air with carbonic acid, such, for example, as respired air, may be effected with sufficient accuracy for most purposes, in the following manner:—Supposing that the gas has been collected over either water or mercury, it becomes necessary to transfer a portion of it from the jar in which it has been collected to the one in which it is to be analysed. A method of effecting this is shown in fig. 243. Upon the board, *a d*, is fastened a pipette, designed for effecting this transfer; *a* is a cylindrical funnel, of a capacity of about two cubic inches; at *c* is a small steel stopcock, by which the contents of the funnel can be admitted to a wide thermometer tube, which is furnished at *d* with a second steel stopcock; *b* is a bulb of the capacity of one cubic inch, or rather less; from the upper part of *b* proceeds another piece of thermometer tube, bent as shown in the figure, to allow of its introduction into the gas-jar. To use the instrument, the funnel, *a*, is filled with mercury, the stopcocks are both opened, and as soon as the air has been displaced from the vertical portion of the fine tube, and mercury escapes through *d*, the stopcock, *d*, is closed; the mercury quickly displaces the air from the rest of the tube, and from the bulb, *b*, and as soon as it begins to flow out at the open extremity of the recurved portion, the stopcock, *c*, is closed. The instrument being now full of mercury, is introduced into the jar, *e*, of the gas, to be transferred, and its open extremity is raised above the level of the water in the jar, *e*; the stopcock, *d*, is then opened, and whilst the mercury runs out into a vessel placed for its reception, the gas enters from *e*, and occupies the place of the mercury in the bulb, *b*. When a sufficient quantity has been admitted, the tube is depressed below the level of the water in the jar, *e*; the stopcock, *d*, is closed, and the pipette, which is sealed by the admission of a little water into the capillary tube, is withdrawn from the jar, *f*. The gas can now be transferred to the graduated tube, *h*, standing in the jar of mercury, as the bent limb of the pipette is introduced into the tube, *h*, which has been previously filled with mercury. Fresh mercury is poured into the funnel, *a*, of the pipette, and on opening the stopcock, *c*, the gas is expelled into the tube, *h*; the gas should not occupy more than two-thirds of the capacity of this tube.

The proportions of carbonic acid, of nitrogen, and of oxygen, are now easily

Carbonic acid constitutes what is termed *choke-damp* by miners, and it often occasions much loss of life after the occurrence of an

ascertained in the following manner:—The bulk of the gas in the tube, *h*, is to be carefully read off, care being taken to bring the mercury to the same level within and without the tube; the temperature and the pressure being observed as usual. Supposing that it has thus been ascertained that a bulk of gas of

FIG. 243.



about two-thirds of a cubic inch is to be subjected to the analysis, the operator, by means of a glass syringe, throws up ten or twelve drops of a solution of caustic potash (sp. gr. 1.4) into the tube. The glass syringe may be extemporaneously prepared from a strong tube, which is softened in the flame of a lamp, drawn off and recurved at one end, as shown in the figure at *i*; this constitutes the body of the syringe, whilst the piston is easily formed of a piece of glass rod, provided with a plug of caoutchouc.

The operator then agitates the contents of the tube, by rapidly thrusting down the tube into the mercury, and withdrawing it; taking care to keep the mouth below the surface of the mercury: this manoeuvre is several times repeated in quick succession; the tube is again left at rest for a minute or two, and the absorption is noted by a second time reading off the volume of the gas at the proper level. The difference indicates the amount of carbonic acid.

In order to ascertain the proportion of oxygen in the remainder, a solution of 1 part of pyrogallie acid in 6 of water is prepared, and about 40 drops of the solution is by a *fresh* syringe injected into the tube *h*, and the mixture is briskly agitated, as before; the solution of potash, if oxygen be present, becomes of an intense bistre colour, and the oxygen is quickly and completely absorbed; the gas is measured a third time, and the residue is estimated as nitrogen; the difference between the second and third readings giving the volume of oxygen.

explosion of carburetted hydrogen, or *fire-damp*. It frequently also accumulates in the old workings of mines, and in pits or wells. Before descending into them, it is usual to lower a candle in order to ascertain whether the light will burn; if it does so, it is generally considered safe to venture down. Instances, however, are on record in which a candle was found burning in an atmosphere which, notwithstanding, contained sufficient carbonic acid to cause death. When it is necessary to enter into an atmosphere considerably charged with this gas, Mr. Graham suggests as a precaution that the mouth and nostrils be covered with a cloth containing a mixture of slaked lime and crystallized sulphate of soda. Such a mixture is porous enough, in a layer of an inch thick, to allow the passage of sufficient air for respiration, whilst the moist lime completely absorbs the carbonic acid.

There is also another mode in which carbonic acid is very largely formed, which, independent of its importance as a source of the gas, is interesting as throwing light upon its chemical nature. Whenever charcoal, or bodies which, like wood, coal, oil, or tallow, contain charcoal, are burned either in oxygen or in air, carbonic acid is obtained abundantly; if the gas, after combustion has terminated, be agitated with lime water, the liquid will be immediately rendered milky.

Carbon may again be extracted from carbonic acid. If a small piece of potassium, heated till it begins to burn in air, be introduced by means of a platinum spoon into a jar of dry carbonic acid gas, the potassium will continue to burn with greater brilliancy. Potash will be formed at the expense of the oxygen which the gas contains, whilst charcoal is liberated, as may be seen in the black particles which are suspended in the water into which the spoon is plunged after the combustion is complete. Thus carbonic acid, both synthetically and analytically, is shown to be a compound substance, consisting of charcoal and oxygen.

Mr. Goldsworthy Gurney has turned the property of extinguishing flame possessed by carbonic acid to an important practical account. Coal mines, at different times and from various causes, are liable to take fire, and from the vast mass of heated matter, the conflagration not unfrequently resists all the ordinary means of checking its ravages; many acres of subterranean fire are thus produced, and the workings are of necessity abandoned. Mr. Gurney in such cases, by the agency of the steam jet, pours into the mine a current of impure carbonic acid and nitrogen, obtained by forcing a stream of air through a coke furnace into the mine, so as to fill the entire workings with the gas, and has thus

on several occasions succeeded at a very small expense in extinguishing fires which have raged unsubdued for years. A very remarkable case of this kind was mentioned in the *Times* for May 22, 1851. The burning waste of Clackmannan, situate about seven miles from Stirling, had been for thirty years on fire. It occurred in a seam of nine-foot coal, and extended over an area of twenty-six acres; the fire was thus successfully extinguished:—about 8,000,000 cubic feet of gas were required to fill the mine, and a continuous stream of impure carbonic acid was kept up night and day for about three weeks. The difficulty lay not so much in putting out the fire, as in cooling down the ignited mass so that it should not again burst into flame on readmitting the air. In order to effect the necessary reduction of the temperature, water was blown in along with the carbonic acid in the form of a fine spray or mist. Subsequently, cold air mixed with the spray was blown in, and in a month from the commencement of operations the fire was found to be completely extinguished.

*Carbonates.*—Though but a feeble acid, the carbonic acid unites with the metallic protoxides, and forms a numerous and important class of salts, which are monobasic; that is, they contain one equivalent of the acid to one equivalent of the base, like carbonate of lime ( $\text{CaO}, \text{CO}_2$ ). In the case of the alkalis a second equivalent of carbonic acid may be combined with the metallic oxide; thus with potash there is a carbonate ( $\text{KO}, \text{CO}_2$ ), and a bicarbonate ( $\text{KO}, \text{HO}, 2 \text{CO}_2$ ). The carbonates, with the exception of those of the alkalis, do not dissolve in water, but many of these insoluble carbonates, and in particular those of lime, magnesia, baryta, and strontia, dissolve to some extent in water charged with carbonic acid, and are deposited in a crystalline form as the gas slowly escapes from the liquid. All the carbonates dissolve with effervescence in dilute nitric acid, or even in acetic acid. The gas which comes off is colourless, and renders lime water turbid, and possesses the properties of carbonic acid, above described. Solution of subacetate of lead is instantly rendered milky by the action of carbonic acid gas upon it. The alkaline carbonates, when in solution, are also decomposed by acids with effervescence; they give with salts of lime a white precipitate, which is immediately re-dissolved by an acid, with effervescence. All the carbonates, with the exception of those of potash, soda, and baryta, are decomposed by prolonged ignition, the acid being entirely expelled from the salt. The carbonates have considerable tendency to combine with each other, and form double salts, like dolomite, which is a double carbonate of lime and magnesia ( $\text{MgO}, \text{CO}_2 + \text{CaO}, \text{CO}_2$ ).

## § II. CARBON.

*Symbol C; Equivalent, 6; Specific gravity as diamond, 3.33 to 3.35.*

(297) Carbon is an elementary body of the greatest importance. Independent of the quantity of it which exists diffused through the atmosphere in the state of carbonic acid, it forms a constituent of the numerous varieties of carbonate of lime and of magnesia, constituting nearly an eighth of the entire weight of the former, and more than a seventh of carbonate of magnesia. It is the characteristic ingredient of all substances which are termed organic; that is, of substances which are produced directly or indirectly from the vegetable or animal creation. The solid parts of plants, shrubs, and trees owe their form and solidity to this element, which is mainly supplied to them from the atmosphere. This action of plants upon carbonic acid is one of the means ordained for preserving uniformity in the composition of the air. The quantities of carbonic acid poured forth from the bowels of the earth, and derived from the processes of respiration and combustion, and from numerous other less apparent sources, would by degrees occasion an injurious accumulation of the gas, but for this compensating action. In solar light the leaves of plants decompose both carbonic acid and water, appropriating the carbon and hydrogen of each for their own growth and nutrition, whilst a large proportion of the oxygen which these compounds contained is returned into the air in the gaseous state. The carbonic acid thus poured out by animals as a refuse and poisonous product, supplies food and sustenance to the vegetable world, which in its turn, converts the carbon into a form suitable for the maintenance of life in animals. Each great division of animated nature is thus seen to be essential to the well-being and even to the support of the other. The fuel which has been burned and dissipated in vapour, is again reduced to the solid state, and by the agency of vegetable life, it is once more fitted for combustion. Plants are in fact the grand agents by which deoxidation is effected, while animals are the channels through which re-combination with oxygen is unceasingly produced.

(298) *Diamond* ( $C_a$ ).—Carbon is found in an uncombined condition in nature under several forms. In its purest state it is met with in the *diamond*, in which it occurs crystallized in forms belonging to the regular system. The crystals are generally derivatives from the octohedron, with a cleavage parallel

to each of the planes of the octohedron, the faces are often convex, and the edges are generally rounded, or *lenticular* as they are termed in such crystals. Diamonds usually present themselves under the appearance of semi-transparent rounded pebbles, enclosed in a thin brownish opaque crust. The gem, when freed from this coating, is generally colourless; such specimens are the most prized; it is, however, met with of various tints, the more common of which are yellow and various shades of brown. The most famous diamond mines are those of Golconda and Bundelcund, in India, of Borneo, and of the Brazils. The origin of the diamond is entirely unknown; it is not probable that it has been formed by crystallization after fusion, as intense heat reduces the diamond to the form of graphite. The circumstances under which diamonds are found in nature afford no clue to the process of their formation. In a solitary instance, in the year 1827, a diamond was found imbedded in a fine grained quartzose rock (*Itacolumite*) in Brazil, but with this exception the gem has been always found to occur scantily in an alluvial matrix, consisting chiefly of sandstone and rolled quartz pebbles, from which they are extracted by washing and careful sorting.

Diamond is the hardest body known: it can only be cut and polished by employing its own powder for the purpose. The fine diamond dust used for this object is mixed with a little olive oil and spread over a revolving steel plate, and the diamond, cemented into a suitable support, has each of its faces in turn presented to the flat face of the disk.\* The most important use to which the diamond is applied is the cutting of sheets of glass; only the natural face of the crystal can be employed for this purpose; crystals with curved faces are the best; they are set in a convenient handle, and a line in the proper direction is traced with the diamond across the glass; slight pressure on each side of the cut, then determines the fracture in the right direction. A true cut is effected by such

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\* The Kohinoor diamond, which was cut in 1852, for the Queen, was imbedded in a copper vessel about the size of a teacup, into which it was cemented with a mixture of equal parts of tin and lead. When it was necessary to change the position of the gem, the solder was melted by immersing the cup, with the diamond imbedded, in a charcoal fire, and heating the metal till it assumed a consistence resembling that of wet sand; in order to cool the diamond more quickly, it was plunged into warm water, and then into cold water; the cutting was effected by means of a cast-iron wheel revolving on a vertical axis about 2400 times per minute; the diamond rested upon the upper surface of the wheel, being held in its position by a kind of vice, and the pressure against the revolving disk was increased or diminished by adding or removing weights. From time to time the face of the diamond was touched with a hair pencil dipped in a cream of diamond dust and oil.

a diamond if properly used, whilst a diamond with angles obtained by cleavage, produces only a superficial scratch with ragged edges. (Wollaston, *Phil. Trans.*, 1816).

The diamond has a very brilliant lustre and a high refracting power; it is a non-conductor of electricity. After exposure to sunshine, many specimens emit a feeble phosphorescent light, which may be seen in a darkened room. The specific gravity of the diamond varies from 3.33 to 3.55. In vessels from which air is excluded, it may be heated intensely without change. If it be suspended in a cage of platinum wire, heated to bright redness, and plunged into oxygen gas, it will burn with a steady red light, and with the production of pure carbonic acid. The diamond, however, is not perfectly pure carbon: it always leaves a minute yellowish ash, which has been found to contain silica and iron (Petzholdt). This ash has generally the form of a cellular network, and may perhaps, at some time, assist in determining the origin of this valuable gem. No heat hitherto applied suffices for the fusion or volatilization of the diamond, or indeed of carbon in any of its forms, though in the intense heat of the voltaic arc, it appears to be mechanically transported from one electrode to the other. When the diamond is introduced into the flame of the voltaic arc it undergoes a remarkable change; as soon as it becomes white hot it begins to swell up, loses its transparency, suddenly acquires the power of conducting electricity, becomes specifically lighter, and is converted into a black opaque mass, resembling coke. The density of a diamond thus altered, was 2.6778, while in its crystalline condition it was 3.336 (Jacquelin, *Ann. de Chimie*, III., xx. 467). The heat of the oxyhydrogen jet was found to be insufficient to produce this change.

(299) *Graphite, or Plumbago*, ( $C_\beta$ ), is a second form in which carbon occurs native. Its most celebrated mine is situated at Borrowdale, in Cumberland, but it is also found in Ceylon, and in several parts of the United States, always in rocks belonging to the earliest formation: the Borrowdale graphite occurs in clay slate; in other localities it is imbedded in gneiss, mica slate, or granular limestone. Graphite occurs either massive or in six-sided crystalline plates belonging to the rhombohedral system. Carbon, in the two forms of diamond and plumbago, offers an excellent instance of dimorphism; the properties which it displays in these two states are as widely different as those of any two dissimilar elements. The specific gravity of graphite varies between 2.09 and 1.8. It has a metallic leaden grey lustre, whence its familiar name of 'black-lead'. It is very friable, and consequently feels



unctuous to the touch, and leaves traces on paper upon which it is rubbed. The particles which compose it are, however, extremely hard, and they rapidly wear out the saws employed to cut it. Graphite is an excellent conductor of electricity. It is never met with in a state free from foreign admixture; when burned in oxygen it leaves from 2 to 5 per cent. of ash, which generally contains quartz and iron; these bodies, however, are merely accidental impurities. The fine-grained amorphous graphite is highly prized for the manufacture of "lead pencils." Where pieces of sufficient size can be obtained they are sawed into thin slices, and these again into small rectangular prisms, which are placed in cedar wood for use. It has been found that the smallest fragments, if of good quality, and the fine powder (which was formerly consolidated by melting it with a minute quantity of sulphur, and was used for the coarser kinds of pencils) may be again reduced into coherent plates by subjecting it to enormous pressure, and may thus be fitted for the manufacture of the best pencils. Black lead is extensively used for lubricating machinery, and as it is quite unaltered by exposure to the weather, it forms a useful coating to protect coarse iron work from rust. An application of graphite which is of some importance to the chemist, is its use in the manufacture of what are termed black-lead crucibles, or blue-pots. The clay used in making them is mixed with a coarse kind of graphite; the pots made from this mixture are much less likely to crack when heated, than if made of fire clay only.

The graphitic modification of carbon may be obtained artificially by several processes. When cast iron is melted in contact with an excess of charcoal, it takes up a considerable quantity of it, and if the iron be allowed to cool slowly, the carbon crystallizes out in the six-sided plates peculiar to graphite. In the manufacture of coal-gas, those parts of the retort which are exposed to the highest temperature, partially decompose the gas as it escapes; a part of the carbon which it held in combination is deposited, and by degrees a layer of very pure, dense carbon is formed, possessed of a lustre resembling that of a metal. The density and appearance of this mass vary according to the temperature to which it has been subjected.

Pit-coal is a substance originally of vegetable origin, which has become altered in appearance and composition by the combined action of heat and moisture under great pressure. It consists largely of vegetable matter in general, of carbon, hydrogen, and oxygen, with a small proportion of nitrogen; and in addition, it contains a variable

quantity of saline and earthy substances, which always exist in the juices of plants. When the coal is burnt in an open fire place, these saline matters are left, and constitute the ashes. When, however, the coal is heated in long closed iron cylinders, so constructed as to exclude atmospheric air, but to allow free escape for volatile matters, a large quantity of gaseous substances, containing the oxygen, hydrogen, and nitrogen, with a part of the carbon of the coal, pass off, while the greater proportion of the carbon remains behind, and constitutes coke. Chemically, it is the same substance as the graphite deposited from the gas, but in a less pure form, owing to the earthy matters which are mixed with it. The higher the temperature to which coke is exposed during its manufacture, the more dense does it become, and the better is it fitted for producing a steady and intense heat, when burned as fuel; though unless the supply of air be tolerably abundant, it burns less freely in this dense condition than when less compact. In order to furnish a coke suited for the use of locomotive engines, it is customary to construct coke ovens. They are usually built of brick, and lined with fire bricks, the walls being from two to three feet in thickness, to economize heat, and this object is further effected by building several ovens together in one continuous piece of masonry. Such an oven twelve feet in internal diameter, and four feet in height, will convert three tons and a half of coal into coke in forty-eight hours. The oven has a sliding door in front, for the purpose of introducing and withdrawing the charge, and for regulating the admission of air, which plays over the surface of the heap and burns off the volatile matters, which escape by a short chimney. The combustion proceeds gradually, from above downwards. In about forty hours after commencing the operation, the door is completely closed, and the furnace left for five or six hours; at the end of that time the coke is withdrawn, and quenched with water. A bituminous coal, like the Newcastle coal, furnishes in this way a very dense lustrous coke, which splits into long columnar masses or prisms, as the temperature in the oven gradually falls, when the door is closed. A fresh charge is introduced into the oven whilst it still remains red hot. The coke in this operation is never melted, and the appearances of fusion which it frequently exhibits are due to the liquefaction, by heat, of the bituminous portions of the coal, previous to their carbonization.

In the fissures of the mass, a very pure form of carbon is frequently observed in black fibres, closely resembling horsehair in appearance. Coke may also be prepared, though with less advantage, by a smothered combustion of the coal in heaps, in a manner

similar to that practised in making charcoal. Coke is subject to great variation in appearance and bulk, according to the kind of coal employed. It is, however, always more bulky than the coal that yields it.

(300) *Charcoal: Amorphous Carbon, (Cγ).*—Carbon also exists in a third form, distinct from that of graphite, and in this state it is amorphous, or entirely destitute of crystalline structure. *Lamp-black* is a variety of this kind of charcoal; it is largely manufactured by heating, in an iron pot, vegetable matters rich in carbon, such as resin or tar; the vapours thus disengaged are kindled and burned in a current of air insufficient for their complete combustion; the hydrogen which these bodies contain, being the more inflammable ingredient, burns off first, leaving the carbon in the form of a very finely-divided powder, such as that which constitutes the visible portion of smoke. The smoky products of this imperfect combustion are made to pass through a large chamber, the walls of which are covered with coarse cloth, and here the lamp-black is deposited. Lampblack always retains a portion of some incompletely burned compounds of carbon and hydrogen. The purest form in which finely divided carbon can be obtained for chemical purposes, is furnished by passing the vapour of turpentine or of ether slowly through tubes maintained at a red heat; a fine powder of charcoal is deposited within them; but this, also, even if again heated intensely in close vessels, always retains traces of hydrogen.

Tinder is another variety of carbon in the amorphous or uncrystalline form; but the most important variety is *Wood Charcoal*, which is largely manufactured by heating billets of wood to dull redness in cast-iron cylinders provided with a tightly fitting lid at one end. The best plan consists in enclosing the wood to be charred in a second lighter case, which can be easily introduced into and withdrawn from the fixed cylinder, which is set in masonry, and protected from the direct action of the flame by a casing of fire-brick. From this kind of iron retort proceeds a tube connected with a condensing apparatus, where the liquid products of the decomposition may be arrested, whilst the uncondensable gases pass on, and are directed into the fire-place, where they are consumed. After the heat has been continued for four or five hours, the end of the outer cylinder is removed, the inner case with its charge is withdrawn, and the whole, whilst still red hot, plunged into an extinguisher or iron case, provided with a tightly fitting lid which protects it from the action of the air; in this condition it is left to cool gradually.

In countries where wood is abundant, the charcoal is manu-

factured by a much ruder method. A plot of ground is levelled in or near the forest, and the logs of wood are piled up regularly round a stake in a mound, which is partially covered up with powdered charcoal, leaves, turf, and earth; the heap is fired from the centre, large quantities of moisture presently exhale, and when the whole mass is thoroughly ignited, it is still more closely covered up from the air, the workmen regulating the admission of air as circumstances require; it is then allowed to burn out. When quite cold, the earth employed to stifle the combustion is removed, and the charcoal is fit for use. The combustion of one part of the wood is thus employed as a source of heat for charring the rest. Charcoal prepared in this manner is, for the purposes of fuel, preferable to that made in cylinders; it is denser and is more completely deprived of volatile matters, because the heat to which it is exposed is much more intense, and is continued for a much longer period. If the diameter of the heap be thirty feet or more, the operation is not complete in less than a month. A slow combustion is found to yield more charcoal than one which is rapidly effected. The resulting charcoal retains the form of the wood, but it is much reduced in size, generally not amounting to more than three-fourths of the bulk of the wood, and never exceeding one-fourth of its weight.

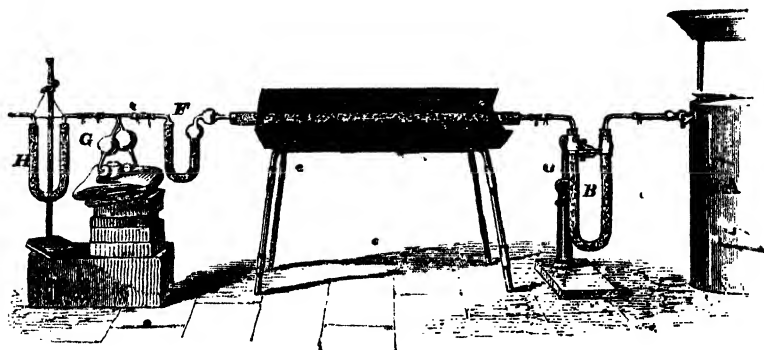
*Animal charcoal*, or ivory black, is prepared in cylinders in a manner similar to that employed for wood charcoal.

(301) *General Properties of Carbon*.—Carbon in all the forms above mentioned is chemically the same. At atmospheric temperatures it is one of those substances in which chemical affinity exhibits least activity; consequently a superficial charring is frequently resorted to to protect wood from decay, as in the case of piles which are driven into mud or into the beds of rivers, to serve as foundations. For the same reason it is a common practice to char the interior of tubs and casks destined to hold liquids. At higher temperatures, the affinity of carbon for oxygen is very energetic. The compounds of carbon with other substances are termed *carburets*, or *carbides*. The diamond is a non-conductor of electricity; in its other forms carbon is an excellent conductor, ranking next to the metals in this respect. In a state of fine subdivision it is a bad conductor of heat, but its conducting power increases with its density. Finely divided charcoal is usually stated to have strong antiseptic powers. It certainly has a remarkable action upon putrescible substances; and Dr. Stenhouse has shown that this action consists in a rapid process of oxidation dependent upon the power of condensing oxygen which charcoal possesses when in a finely divided state. Animal matter in an advanced state of putrefaction loses all offen-

sive odour when covered with a layer of charcoal; it continues to decay, but without emitting any ill odour, till at length all the carbon is dissipated as carbonic acid, the hydrogen as water, and the nitrogen remains as nitric acid. Its remarkable power of absorbing various bodies, particularly colouring matters and many bitter principles, when in a finely divided state (53), as well as its property of condensing a large proportion of gaseous matters within its pores (62), have been already mentioned. So rapid is this action, that Dr. Stenhouse has proposed to use a respirator filled with charcoal, to protect the mouth and nostrils in an infected atmosphere; and the employment of trays of powdered wood-charcoal in dissecting-rooms, in the wards of hospitals, and in situations where putrescent animal matter is present, is found to exert a most beneficial influence in sweetening the atmosphere by absorbing and decomposing the offensive gases. These properties render charcoal a valuable material in the construction of filters, not only for decolorizing purposes, but also for assisting in purifying water for domestic use. At high temperatures carbon combines rapidly with oxygen, and will remove it from a great number of its compounds, especially from the oxides of the metals; hence the various forms of carbon are very extensively employed in the reduction of these substances to the metallic condition.

(302) *Synthesis of Carbonic Acid*.—As a knowledge of the composition of carbonic acid is a fundamental datum for the analysis of organic compounds, the proportion in which oxygen combines with carbon to produce carbonic acid has been determined with the greatest care by the combustion of weighed quantities of diamond, of graphite, and of charcoal, in a stream of dry oxygen. The apparatus employed for this purpose is represented in fig. 244. A represents a gas-holder filled with oxygen; B a tube containing

FIG. 244.



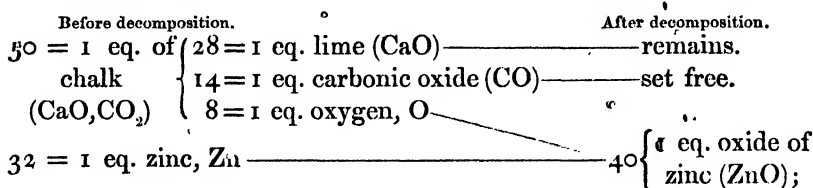
fragments of caustic potash, or pumice-stone moistened with sulphuric acid, for removing all traces of moisture from the oxygen; *c d* is a tube of hard glass traversing the sheet iron furnace. At *c* is a platinum tray containing the weighed portion of diamond or graphite; the front of the tube *d* is occupied by a column of oxide of copper. The apparatus is filled with dry oxygen, by opening the stopcock of the gas-holder, *A*, to a regulated distance, and the fore-part of the tube, *d*, is brought to red heat by means of lighted charcoal; the heat is then applied to the spot, *c*, where the carbon lies. The carbon burns and becomes converted into carbonic acid, which passes on through the column of heated oxide of copper; *f* is a weighed tube, filled with chloride of calcium, which, if water were present, would be found to increase in weight, but in which no deposit of moisture is formed if the experiment be properly conducted. The carbonic acid passes on, and is absorbed by a strong solution of potash which is contained in the bulbs of the Liebig's apparatus, shown at *g*. The excess of oxygen absorbs moisture as it passes through this liquid, but before it is allowed to escape into the air it is rendered perfectly dry by causing it to pass through an additional tube, *h*, filled with fragments of caustic potash. The increase in weight acquired by the tubes *g* and *h* furnishes the weight of the carbonic acid corresponding to the quantity of carbon consumed, and the quantity of carbon burned is ascertained by weighing the platinum tray and its contents after the experiment has terminated. In this way it has been determined that 6 parts of carbon require for conversion into carbonic acid exactly 16 parts of oxygen (Dumas and Stas, *Ann. de Chimie*, III. i. 5).

If a piece of pure carbon be burned in a jar of oxygen over mercury, it will be found after the combustion is over, and the gas has cooled to its original temperature, that its volume has undergone no permanent change: the bulk of the oxygen, therefore, is not altered by this combination; the carbonic acid which is formed occupies precisely the same space as the oxygen which produced it.

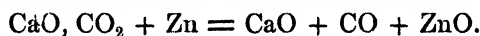
Diamond, graphite, and charcoal, are chemically the same substance, and yet differ entirely in properties, these three conditions being *allotropic* modifications of carbon, the differences in properties arising not from differences in their chemical nature, but in their molecular arrangement.

(303) *Carbonic Oxide*, (CO); *Equivalent*, 14; *Specific Gravity*, *Combining Volume*, 2.—It has been shown that carbonic acid is wholly deprived of its oxygen when heated with potassium; but if some metal, such as zinc or iron, which has a less powerful affinity for oxygen, be substituted for the potassium, the carbonic

acid will only be partially deoxidized; the metal will deprive it of exactly half the oxygen which it contains, and a new gaseous body, termed carbonic oxide, will be produced. The bulk of this new gas is exactly equal to that of the carbonic acid that furnished it. Carbonic oxide may be conveniently prepared by mixing powdered chalk with an equal weight of iron or of zinc filings, and exposing the mixture to a red heat in a gun barrel. The chalk when ignited gives off carbonic acid, which in contact with the heated metal is decomposed; oxide of iron or of zinc is formed, quick lime remains in the retort mixed with the metallic oxide, and the carbonic oxide gas may be collected over water, in which it is but slightly soluble. These chemical changes may be presented in the following manner:—



or the decomposition may be thus briefly represented in symbols:—



The chemical composition of carbonic oxide may be ascertained in the following manner:—Introduce into the bent eudiometer (fig. 239) a certain measure, say 20 parts, of carbonic oxide, then add 20 measures of pure oxygen; pass the electric spark with the precautions already described: the 40 measures of gas will diminish to 30 measures. If a little solution of potash be introduced, 20 measures of the residual gas will disappear, leaving 10 measures of unaltered oxygen: the 20 measures of gas absorbed are carbonic acid. Now carbonic acid contains its own bulk of oxygen, but the 20 measures of carbonic oxide required only 10 measures, or half its bulk of oxygen to convert it into carbonic acid. Carbonic oxide therefore must have contained the other 10 measures of oxygen; in other words, half its bulk of oxygen. But the specific gravity of carbonic oxide

is 0.9674 deduct from this

0.5528 = half the density of oxygen

0.4146 the remainder is the weight of the carbon  
combined with 0.5528 of oxygen.

Now 0.5528 : 0.4146 :: 8 : 6. The proportion by weight of oxygen to carbon in carbonic oxide is therefore 8 : 6, or 4 equivalent of each.

*Properties.*—Carbonic oxide is a transparent, colourless gas, with a faint oppressive odour. It is much lighter than carbonic acid, having a specific gravity of 0.967 (Wrede). All attempts at its liquefaction have as yet been unsuccessful. When respired, even though diluted with air, it acts as a direct poison, producing a peculiar sensation of oppression and tightness of the head. It does not support combustion, but burns itself with a beautiful pale-blue light, producing by its combination with oxygen carbonic acid only. A solution of dichloride of copper in hydrochloric acid, or of the salts of dioxide of copper in ammonia, rapidly absorbs carbonic oxide if agitated with it. Carbonic oxide is absorbed by potassium if the metal be gently heated in the gas, 7 equivalents of carbonic oxide combining with 3 equivalents of potassium. This property is sometimes employed for separating carbonic oxide from its mixture with other inflammable gases, in the process of analysing mixtures of such gases.

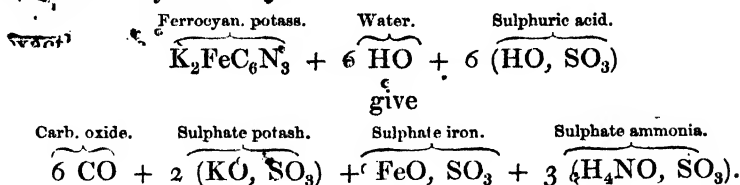
Although carbonic oxide shows but little tendency to combine directly with other substances, it has been supposed to form the basis or radicle of a numerous series of compounds; the probability of this view, however, is but slight.

Carbonic oxide is often produced abundantly in the ordinary process of combustion in stoves and furnaces: this mode of its formation is important, as it exercises a material influence upon the economy of combustion, and in many metallurgic operations the carbonic oxide so produced plays a conspicuous part in the reduction of the ore to the metallic state. The formation of carbonic oxide in an open fire which is burning steadily without emitting smoke is often evidenced by the flickering blue flame seen playing over the glowing embers. In this case carbonic acid is first formed at the bottom of the grate from the free access of air to this part of the burning fuel; the carbonic acid gas as it traverses the red-hot coke enters into combination with an additional quantity of carbon. The acid, by losing half its oxygen, is converted into its own bulk of carbonic oxide, and at the same time the carbon of the heated fuel which has entered into combination with this removed oxygen furnishes another equal quantity of the same gas: and the heated carbonic oxide takes fire as soon as it mixes with the air which passes over the upper surface of the fire. The reaction between the hot carbon and carbonic acid may be thus represented:  $\text{CO}_2 + \text{C} = 2 \text{CO}$ .

Carbonic oxide may also be formed in several other ways. Half an ounce of the yellow prussiate of potash, finely powdered, placed in a retort, and heated with four or five ounces of oil of vitricl, yields more than a gallon of the pure gas (Fownes). The

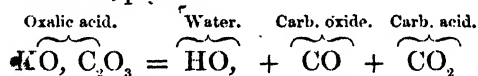


reaction is in this case of a complicated nature, but is expressed by the annexed symbols:—



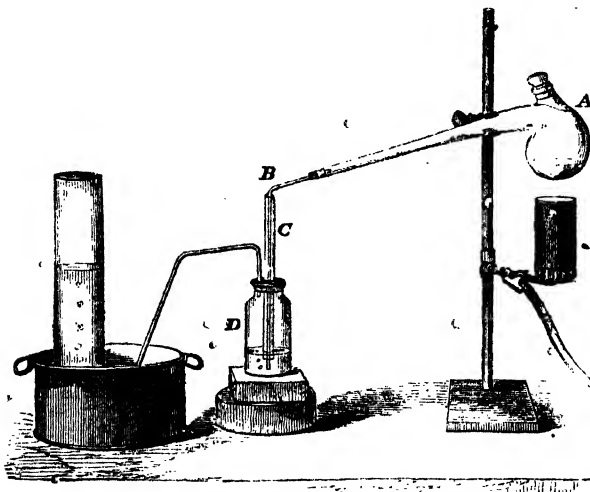
One equivalent of ferrocyanide of potassium and 9 equivalents of water produce 6 equivalents of carbonic oxide, 2 of potash, 1 of protoxide of iron, and 3 equivalents of ammonia; and these bases all combine with sulphuric acid to form sulphates, some of which afterwards form double salts with each other.

Another method by which carbonic oxide may be obtained with facility consists in decomposing oxalic acid by means of oil of vitriol. By the application of a gentle heat, one equivalent of oxalic acid is deprived of water and is resolved into a gaseous mixture consisting of equal measures of carbonic acid and carbonic oxide; by allowing the mixed gases to pass through a vessel filled with solution of potash, the carbonic acid is absorbed, and the carbonic oxide may be collected in a state of purity. The decomposition may be thus explained:—



A convenient mode of washing the gas is shown at B fig. 245, the

FIG. 245.



bent tube is connected to the neck of the retort, *a*, and passes to the bottom of a wider tube, *c*, open both at top and bottom, which passes into the washing bottle, *d*: a moveable gas-tight joint, which can be mounted or dismounted in a moment, is thus obtained.

Carbonic oxide and carbonic acid, widely as they differ in properties, consist, it is evident, of the same elements; but the proportion of the two elements is different in the two cases. Carbonic oxide is the compound of carbon that contains the smallest proportion of oxygen; 3 parts by weight of carbon are united in this gas with 4 of oxygen, or comparing the quantity of oxygen with the proportion combined with 1 part of hydrogen to form water, 6 of carbon are in carbonic oxide united with 8 of oxygen. In carbonic acid, on the other hand, the proportion of carbon is 6 parts by weight of carbon to 16 of oxygen. Carbonic oxide has been regarded as a compound of 1 equivalent of carbon and one of oxygen, and is represented by the symbol  $\text{CO}$ , whilst carbonic acid is regarded as a compound of 1 equivalent of carbon and 2 equivalents of oxygen, and it is represented as  $\text{CO}_2$ . The equivalent number of carbon will therefore be 6 if that of hydrogen be assumed as 1.

## CHAPTER V.

### COMPOUNDS OF NITROGEN WITH OXYGEN AND HYDROGEN.

#### § I. COMPOUNDS OF NITROGEN WITH OXYGEN.

THE affinity of nitrogen for oxygen is much feebler than that of either carbon or hydrogen, so that it is not easy to procure their direct union,—especially as the temperature emitted by nitrogen and oxygen in the act of combination is comparatively low. Nitrogen, notwithstanding, forms with oxygen five distinct compounds, containing, respectively, 1, 2, 3, 4, and 5 equivalents of oxygen with 1 equivalent of nitrogen.

These compounds have been named

		Composed by weight, of		
		14 Nitrogen +	8 Oxygen.	
Protoxide of Nitrogen,	$\text{NO}$ ,	14	8	
Deutoxide of Nitrogen,	$\text{NO}_2$ ,	14	+ 16	„
Mitox acid,	$\text{NO}_3$ ,	14	+ 24	„
Peroxide of Nitrogen	$\text{NO}_4$ ,	14	+ 32	„
Nitric acid	$\text{NO}_5$ ,	14	+ 40	„

(304) NITRIC ACID,  $(\text{NO}_3)_2$ ; *eq.* 54.—Of these compounds the last, the nitric acid, formerly called aquafortis, is the most important. It was known to the alchemists, but its true composition was first determined by Cavendish, in 1785. When nitrogen is mixed with twelve or fourteen times its bulk of hydrogen, and a jet of the mixed gas is allowed to burn in air or in oxygen, water is formed, which has a sour taste and an acid reaction, from the simultaneous formation of a small quantity of nitric acid. In this case, the nitrogen burns by the aid of the heat developed during the combustion of the hydrogen, and the nitric acid combines at once with the water formed, which much increases its chemical stability. It was, indeed, owing to the accidental production of nitric acid in the course of his experiments on the formation of water by the combustion of hydrogen, that Cavendish was induced to institute the train of research which terminated in this important discovery. If 2 vols. of nitrogen be mixed with 5 vols. of oxygen, in an inverted syphon containing a few drops of infusion of litmus, each limb plunging into a separate glass of mercury, and a series of electric sparks be passed through the mixture, the two gases will slowly combine, and the litmus will be reddened. The heat of the spark determines combination of the gases just at the spot through which it passes, but the action does not extend further. In like manner, if a number of sparks be passed from the electrical machine, between two metallic points, over moistened litmus paper, in air, a red spot will be produced upon the paper, owing to the formation of nitric acid in minute quantity by the combination of oxygen with nitrogen. During stormy weather, and indeed whenever a flash of lightning passes through a moist atmosphere, the same compound is produced in appreciable quantity. Indeed, it is rare to meet with rain water in which traces of nitrate of ammonia may not be detected, if the experiment is made with sufficient attention to accuracy.

Nitric acid also occurs in combination with potash or soda, in the form of an efflorescence on the soil, especially in tropical climates, as in some parts of India and Peru. The compound formed with potash constitutes the nitre or saltpetre of commerce.

*Preparation.*—It is from one of these nitrates that the acid is always obtained for chemical purposes. When nitre is heated with a powerful acid, such as the sulphuric, it is decomposed; a combination of sulphuric acid with potash remains in the retort, whilst the more volatile nitric acid distils over, and may be condensed in the usual manner. In preparing nitric acid on the small scale, equal weights of nitre and strong oil of vitriol are placed in

a glass retort, and the distillation is proceeded with in the manner shown in fig. 109, Part I., p. 236. The result of the reaction may be traced as follows:—

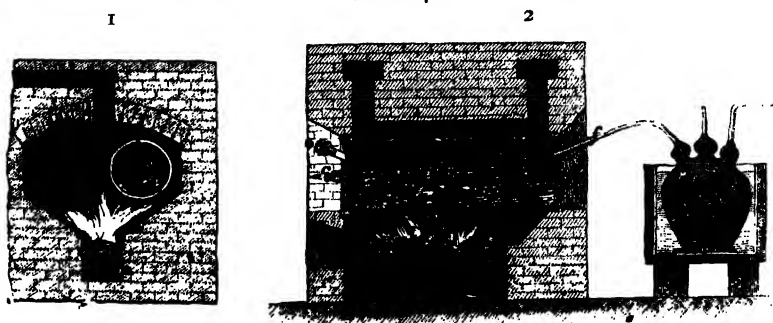
$\text{KO}, \text{NO}_5 + 2 (\text{HO}, \text{SO}_3)$  give  $\text{HO}, \text{NO}_5 + (\text{KO}, \text{HO}, 2 \text{SO}_3)$ ; or, as it may be illustrated more in detail,

Before decomposition.		After decomposition.	
101 = 1 eq.	Nitrate of Potash	63	1 eq. Liquid nitric acid.
54 = 1 eq.	Nitric acid		
47 = 1 eq.	Potash		
98 = 2 eqs.	Water		
	Oil of vitriol	136	1 eq. Bisulphate of potash.

During the distillation red fumes appear in the retort, arising from a partial decomposition of the acid, and a formation of some of the lower oxides of nitrogen. In the receiver a yellowish corrosive liquid condenses, which fumes strongly in the air, and emits a powerful, irritating odour. On the large scale, iron retorts, fig. 246, coated with fire clay on the inside of the upper part, where they are exposed to the acid vapours, are employed for the distillation, and nitrate of soda is substituted for nitrate of potash, as it is a cheaper salt, and likewise contains 9 per cent. more nitric acid than nitrate of potash.

The cylinders or retorts are arranged in pairs in a furnace, so that each fire heats two cylinders, as shown in the section 1.

FIG. 246.

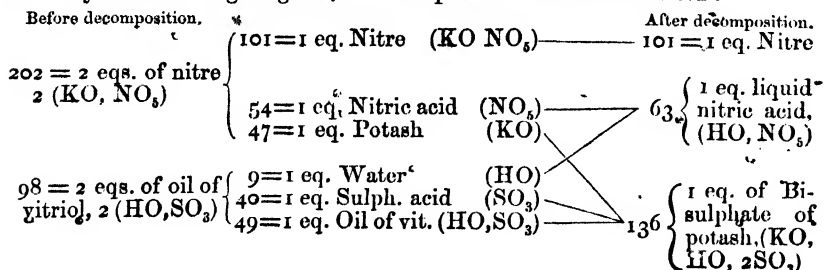


The cylinders are supplied with a moveable lid, *c d*, at each end. The nitrate is introduced into the retort, *A*, through the opening at *c*, which is closed during the distillation by a stone lid, which fits the aperture accurately; the oil of vitriol being introduced by a funnel at *e*, after the retort is closed. As soon as the

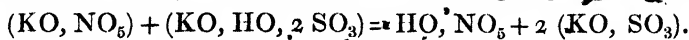
acid is introduced, the funnel is withdrawn, and the opening closed with a plug. The acid as it distils over passes through the pipe *f*, and is condensed in a series of stoneware bottles, the first of which is seen at *B*. The acid which condenses in the first receiver is always contaminated with sulphuric acid, and that in the last is rather dilute, as water is placed in it to condense the nitrous fumes.

It is usual upon the large scale to employ a smaller quantity of sulphuric acid, than when the distillation is performed in glass vessels, as it is quite possible to effect a complete decomposition of the nitrate by heating it with one-half its weight of oil of vitriol. Under these circumstances, however, a higher temperature is needed to expel the last portions of acid, and a considerable quantity of the nitric acid is thereby decomposed and wasted. The residue in the retort, when the smaller quantity of sulphuric acid is used, is much less soluble in water, and consequently is much more difficult of removal: in the iron cylinder of the manufacturer this is of no moment, as the saline mass can easily be detached by the use of iron tools when the distillation is at an end. The cause of these differences lies in the fact, that sulphuric acid forms with potash two different compounds, one of which contains twice as much acid as the other. When nitre and sulphuric acid are mixed in the proportion of 2 equivalents of each, half the nitre only is decomposed, so long as a gentle heat only is employed, and the acid sulphate of potash is formed. The nitric acid thus liberated, distils over readily. The following symbols show the form of this reaction.\*  $2(\text{KO}, \text{NO}_3) + 2(\text{HO}, \text{SO}_3)$  give  $(\text{KO}, \text{NO}_3) + (\text{HO}, \text{NO}_3) + (\text{KO}, \text{HO}, 2\text{SO}_3)$ . As soon as the first half of the nitric acid has passed over, the temperature begins to rise, and the acid sulphate of potash then reacts on the undecomposed nitre; the second half of the nitric acid is liberated, but at the same time is partially decomposed towards the end of the operation, and the whole of the potash remains in combination with sulphuric acid

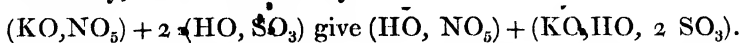
\* The symbols employed in the equation will perhaps be more easily understood by the following diagram, which represents the same reaction:—



in the form of the sparingly soluble neutral sulphate. This second stage of the decomposition is exhibited in the subjoined equation, which will be easily understood from the foregoing explanation.



When, on the other hand, 2 equivalents of sulphuric acid are used to 1 of nitre, the whole of the potash is at once converted into the acid sulphate, so that the whole of the nitric acid is liberated immediately, and distils readily.



*Properties.*—Nitric acid, in the most concentrated form in which it can by this process be obtained, is, when pure, a colourless, limpid, fuming, powerfully corrosive acid liquid, of sp. gr. 1.520. It is the highest oxide of nitrogen known to exist, and contains 1 equivalent of nitrogen with 5 of oxygen, combined with 1 equivalent of water ( $HO, NO_5$ ). 100 parts of this liquid contain 85.72 of the anhydrous nitric acid. It is very readily decomposed, as mere distillation always produces its partial decomposition. Exposure to the light of the sun has a similar effect. At  $184^\circ$  it begins to boil, and freezes about  $-40^\circ$  F. Nitric acid very readily parts with a portion of its oxygen to the metals, and to combustible bodies. If it be dropped into hot finely powdered charcoal, the charcoal burns vividly; if mixed with a little oil of vitriol and poured into oil of turpentine, the mixture bursts into flame. Nitric acid acts violently upon tin or iron filings, especially if they be previously moistened with a few drops of water: the acid is indeed constantly employed by the chemist as an oxidizing agent.

The action of nitric acid upon the metals is instructive, and it may serve to illustrate the manner in which metallic bodies combine with the acids generally. The metals will enter into direct combination with many of the simple non-metallic bodies: thus antimony will unite directly with chlorine, and will even take fire if allowed to fall into this gas in fine powder. Iron will burn in oxygen: and copper turnings, if mixed with powdered sulphur, will combine with the sulphur on the application of heat, emitting a vivid glow of light. But no metal will unite directly with an acid; in order that combination between them should occur it is necessary that the metal should be in the form of oxide. This oxidation may, however, be effected at the same time that the acid is presented to the metal, and the formation of the oxide and its solution in the acid may appear to occur simultaneously. Zinc, for example, does not unite as zinc with sulphuric acid: when this metal is placed in dilute sulphuric acid, the oxygen is supplied from the

water which is decomposed, oxide of zinc is produced, and is immediately dissolved by the acid, whilst the hydrogen escapes in the gaseous form. When a metal such as copper or silver is dissolved by nitric acid, a preliminary oxidation is equally necessary; but owing to the facility with which nitric acid is deprived of a part of its oxygen, this oxidation is usually effected at the expense of the nitric acid, which is decomposed more readily than water is; some of the lower oxides of nitrogen are liberated in the form of ruddy fumes, whilst the compound of the metal with oxygen dissolves in another portion of the acid which has not undergone decomposition. The exact nature of the decomposition which the nitric acid experiences varies in different cases. Silver when allowed to dissolve slowly in the cold, in dilute nitric acid, produces nitrous acid ( $\text{NO}_2$ ) which remains in solution: thus  $2 \text{Ag} + 3 \text{NO}_5$  becomes  $2 (\text{AgO}, \text{NO}_5) + \text{NO}_3$ , and the metal dissolves without evolution of gas; and a similar effect is produced by palladium. With metals which, like copper and mercury, have a somewhat stronger affinity for oxygen, deutoxide of nitrogen ( $\text{NO}_2$ ) is disengaged in large quantity; for example,  $3\text{Cu} + 4 \text{NO}_5 = \text{NO}_2 + 3 (\text{CuO}, \text{NO}_5)$ : and if the metal have a still more powerful tendency to combine with oxygen, as is the case with zinc, the protoxide of nitrogen ( $\text{NO}$ ) is, if the acid be dilute, amongst the gases disengaged:  $4 \text{Zn} + 5 \text{NO}_5$  would produce  $\text{NO} + 4 (\text{ZnO}, \text{NO}_5)$ . Zinc and tin also decompose water as well as nitric acid when dissolved in the acid, setting hydrogen free, and the hydrogen at the moment of its liberation completely deprives a portion of nitric acid of its oxygen, and forms ammonia ( $\text{H}_3\text{N}$ ), by entering into combination with the liberated nitrogen; for instance,  $8 \text{Zn} + 8 \text{HO} + 8 \text{NO}_5 = 8 (\text{ZnO}, \text{NO}_5) + 8 \text{H}$ , and  $\text{NO}_5 + 8 \text{H}$  yield  $5 \text{HO} + \text{H}_3\text{N}$ . In order to produce a rapid oxidation of the metals it is best to dilute the acid until it has a specific gravity between 1.25 and 1.35; the action is then very brisk. Nitric acid is one of the most corrosive substances known: it turns wool, feathers, the skin, and all animal matters containing albumen, of a bright yellow colour. When the concentrated acid is exposed to the air, it absorbs moisture; and if mixed with water it emits a sensible amount of heat, owing to the formation of another hydrate of much greater stability.

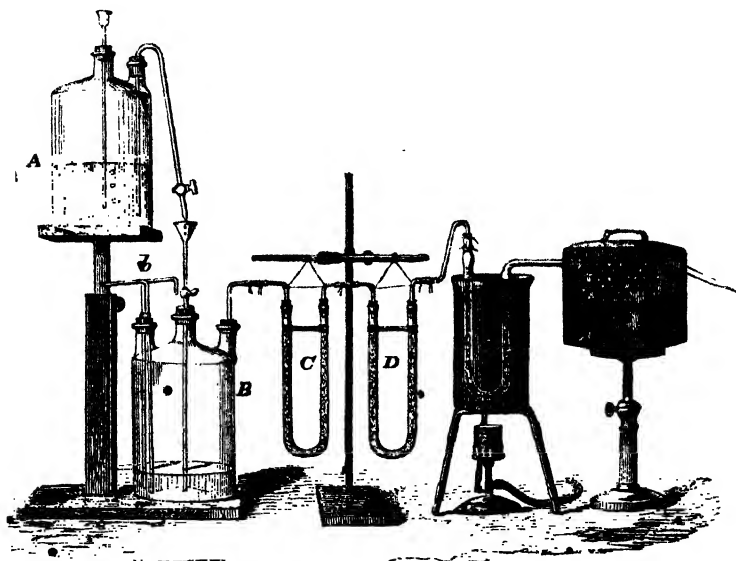
This stable hydrate contains 4 equivalents of water and 1 of nitric acid ( $\text{HO}, \text{NO}_5 + 3 \text{aq}$ ): it has a specific gravity of 1.424, and is composed of 60 per cent. of anhydrous acid, and 40 of water. This hydrate has a higher boiling point than the protohydrate, and distils at  $250^\circ$  without change. A weaker acid parts with its water when heated, till it arrives at this density, and a stronger

acid, in like manner, loses acid; the liquid in the retort being eventually, in both cases, reduced to the hydrate with 4 equivalents of water, of sp. gr. 1.424. According to Binçay, the vapour of this hydrate has a density of 1.243. Ten volumes of this vapour contain 1 equivalent of the acid.\*

*Anhydrous Nitric Acid.*—Nitric acid may be obtained in an anhydrous condition (Deville, *Ann. de Chimie*, III. xxviii. 241), in which state it forms perfectly transparent, brilliant, colourless crystals, derived from the right rhombic prism: they melt at  $85^{\circ}$  and boil at  $113^{\circ}$  F.: about this temperature the compound begins to undergo decomposition. Sometimes the crystals, even if kept in sealed tubes, undergo decomposition at the ordinary atmospheric temperature, and the tube bursts with a dangerous explosion from the pressure exerted by the liberated gases. The crystals dissolve rapidly in water, emitting much heat, and producing ordinary nitric acid.

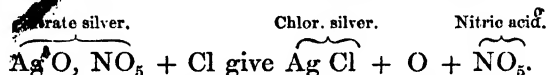
Anhydrous nitric acid may be prepared by passing a uniform current of perfectly dry chlorine gas very slowly over crystals of well dried nitrate of silver; the salt is heated to about  $200^{\circ}$  at first, till the decomposition has commenced, and the temperature is then lowered to about  $150^{\circ}$  F. The operation is one of considerable delicacy, and requires attention to a number of minute precautions, for the details of which the reader is referred to M. Deville's paper. The apparatus required is shown in fig. 247. A is a vessel of concentrated sulphuric acid: the acid is drawn off from it by means of the syphon, and allowed

FIG. 247



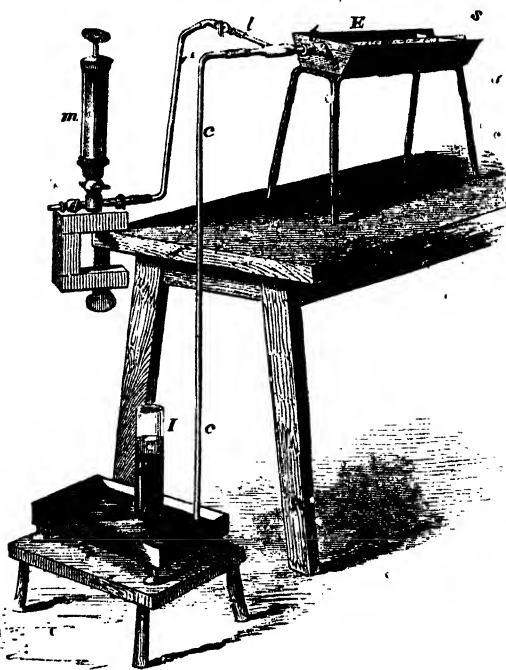


to flow into the vessel B, in a very slender stream, which can be regulated by the glass stopcock; B has also been filled with sulphuric acid, and subsequently charged with pure dry chlorine by means of the bent tubes at *b*. *c* is a tube filled with dry chloride of calcium; *d* a tube filled with pumice moistened with sulphuric acid; *e* a wide tube filled with nitrate of silver in crystals, immersed in a bath of oil; *f* the receiver for the anhydrous nitric acid, which is kept cool by a freezing mixture of ice and salt. The tubes, *e* and *f*, are made of one continuous piece of glass, as the acid immediately attacks and destroys cork or caoutchouc joints: a portion of one of the lower oxides of nitrogen is liquefied and collects in the bulb in *f*, and is thus separated. The chlorine displaces the nitric acid and oxygen from the nitrate of silver; chloride of silver is formed, and the nitric acid and oxygen escape. By surrounding the receiver, *f*, with a freezing mixture, the nitric acid is condensed in crystals. The decomposition is of the following simple character:—



The composition of anhydrous nitric acid was determined by

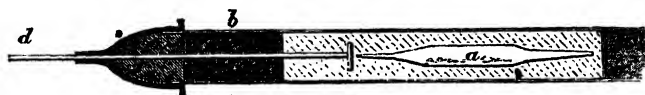
FIG. 248.



M. Deville, by estimating the quantity of nitrogen which a given weight of the acid furnished after the oxygen had been removed from it by heating it in contact with copper, which rapidly combines with the oxygen at a high temperature. The experiment was conducted as follows:—Having transferred into a small tube (*a*, fig. 249), the weight of which is accurately known, 7 or 8 grains of the crystals, the capillary tubes are closed, and the

weight again determined exactly; a tube, *s t*, of hard glass, from twenty-four to thirty inches long, and open at both ends, is filled for about two-thirds of its length with copper turnings; the little tube, *a*, of nitric acid is then introduced; metallic copper in a state of fine subdivision is then carefully packed around the tube, *a*, and the remaining portion, *b*, of the long tube, *s t*, is filled up with a mixture of bicarbonate of soda and finely divided copper. The tube, *s t*, may now be placed in a long sheet-iron furnace, *e*, fig. 248; one limb of the three-branched glass tube, *l*, is attached by means of a sound cork to the end, *t*, of the tube *s t*; to another limb of the piece, *l*, a caoutchouc joint connects the bent tube, *c c*, which is upwards of thirty inches long, and is designed to convey the gases produced in the course of the operation into a graduated jar, *r*, standing in the mercurial bath. The upper part of this jar contains a small quantity of a strong solution of potash. Into the end, *s*, of the long tube, shown upon an enlarged scale in fig. 249, is a second

FIG. 249.



cork and tube of caoutchouc, through which a glass rod, *d*, slides stiffly; the object of this rod is to enable the operator to break the end of the little tube, *a*, and liberate the vapours of the nitric acid when everything is prepared. It is necessary first to get rid of the air which the apparatus contains. For this purpose the third limb of the piece, *l*, is connected with an exhausting syringe, *m*, the air withdrawn, and the tube, *l*, sealed by the blowpipe or closed by a stopcock. A few pieces of lighted charcoal are introduced into the sheet-iron furnace, *e*, and applied near the end, *s*, to disengage the carbonic acid gas from the bicarbonate of soda; this gas gradually sweeps out the remaining traces of air from the apparatus, and when at length the bubbles which escape through the tube, *c*, are wholly absorbed by a solution of potash, the air may be considered to have been expelled. Care is taken not to decompose the whole of the bicarbonate of soda at this stage of the process, as a portion will be required to sweep out the gas left in the tube after the operation is complete. The copper in the front of the tube is now heated by placing ignited charcoal around it, and the point of the little tube, *a*, is broken by thrusting the blunt end of the rod, *d*, against it; the vapour of the nitric acid passes slowly over the heated copper, by which the acid is decom-

posed; the oxygen is wholly absorbed by the copper, and the nitrogen passes into the mercurial jar, 1. When the decomposition is concluded, the gas which remains in the glass tube, &c., is swept into the jar, 1, by carbonic acid, which is obtained by heating the remainder of the bicarbonate of soda. The carbonic acid is entirely absorbed by the potash, and pure nitrogen remains; the volume of this gas is carefully measured, and corrected according to the temperature and the pressure of the air; then the weight of the nitrogen is easily calculated. M. Deville found in one of his experiments that 547 milligrammes of acid gave 116 cubic centimetres of gas at a temperature of  $5^{\circ} \cdot 2$  C. whilst moist and under a barometric pressure of 757 millimetres. This, when corrected, gives in 100 parts of the acid by weight, 25.9 of nitrogen; the deficiency, 74.1, is oxygen: or 14 parts of nitrogen are united with 40 of oxygen.

(305) Hydrated nitric acid is liable to be contaminated with a variety of impurities, of which sulphuric acid, chlorine, potash, and oxide of iron are the most frequent. Its usual yellow or red colour is owing to the presence of the lower oxides of nitrogen. It should leave no fixed residue when evaporated on a slip of glass, and give no precipitate when diluted with three or four times its bulk of water, and tested for sulphuric acid with nitrate of baryta, and for chlorine with nitrate of silver. It may readily be obtained free from all impurities, except the lower oxides of nitrogen, by distilling it a second time; if chlorine be present, nitrate of silver may be added previously, so long as the silver salt occasions a precipitate; or a silver coin may be dissolved in the acid, after which the rectification may be proceeded with.

*Nitrates.*—Nitric acid combines with one equivalent of the various bases to form the class of salts termed nitrates: no acid nitrates are known to exist, but several subnitrates may be formed; that is to say, salts may be formed which contain more than one equivalent of base for each equivalent of acid; such for instance, as subnitrate of copper ( $3 \text{ CuO}, \text{NO}_5, \text{HO}$ ). When heated, most of the nitrates fuse readily: at an elevated temperature they are all decomposed, and in most cases the pure oxide of the metal is left. When thrown on glowing coals, the nitrates are decomposed with scintillation; if dissolved in water, and paper be moistened with the solution, allowed to dry, and then burned, the smouldering combustion characteristic of touch-paper will be produced. This property is however also exhibited by the salts of some other acids of which the chloric is the most important.

• There is no ready method of precipitating nitric acid from its solutions, since all its compounds dissolve in water more or less

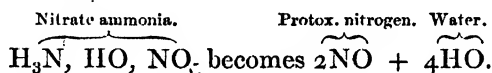
freely. Various indirect methods have been proposed for ascertaining its presence. One of the best consists in neutralizing the solution, if acid, with potash, and evaporating nearly to dryness; then adding a few copper clippings, and heating the mixture with a little oil of vitriol. The copper combines with a portion of the oxygen of the nitric acid, and decomposes the acid, and characteristic red fumes of peroxide of nitrogen show themselves, if nitric acid be present. A still smaller quantity of the acid may be detected by substituting a crystal of green sulphate of iron for the copper, before adding the oil of vitriol: on the application of a gentle heat in this case, the characteristic action consists in the formation of an olive green solution, the colour of which disappears on boiling; the nitrous acid gas, formed by the deoxidizing action of one portion of the iron salt, dissolves, with the distinctive green colour, in the solution of the unoxidized part of the salt. If a few drops of hydrochloric acid be added to a solution which contains free nitric acid, or a nitrate in solution, the liquid acquires the power of dissolving gold leaf. This effect, however, is produced by hydrochloric acid in solutions of the iodates, chlorates, and bromates, but the presence of these salts may be detected by other characters.

The following is an abridgment of a table giving the per-centage of anhydrous nitric acid contained in aqueous solutions of nitric acid of various specific gravities, as determined by Dr. Ure.

Specific gravity.	NO <sub>3</sub> in 100 parts by weight.	Specific gravity.	NO <sub>3</sub> in 100 parts by weight.
1.5000	79.700	1.2887	39.053
1.4940	77.303	1.2705	36.662
1.4850	74.918	1.2523	34.271
1.4760	72.527	1.2341	31.880
1.4670	70.136	1.2149	29.489
1.4570	67.745	1.1958	27.098
1.4460	65.354	1.1770	24.707
1.4346	62.963	1.1587	22.316
1.4228	60.572	1.1403	19.925
1.4107	58.181	1.1227	17.534
1.3978	55.790	1.1051	15.143
1.3833	53.399	1.0878	12.752
1.3681	51.068	1.0708	10.361
1.3529	48.617	1.0540	7.970
1.3376	46.226	1.0375	5.579
1.3216	43.835	1.0212	3.188
1.3056	41.444	1.0053	0.797

(306) PROTOXIDE OF NITROGEN, or *Nitrous Oxide*, (NO); *Equivalent*, 22; *Specific Gravity*, 1.527; *Combining Volume*, 2.—If nitric acid, diluted with about 16 parts of water, be digested on metallic zinc, the metal deoxidizes the acid, and a colourless gas is given off,

composed of 1 equivalent of nitrogen united with 1 equivalent of oxygen : but to obtain the gas in a pure state it is better to heat nitrate of ammonia ( $\text{H}_4\text{NO}_3\text{NO}_5$ ), (the salt furnished by neutralizing pure nitric acid with carbonate of ammonia) in a glass retort ; the salt quickly melts, and at a temperature of between  $400^\circ$  and  $500^\circ$  apparently begins to boil, but in reality it is undergoing decomposition, by which it is entirely resolved into the gaseous protoxide of nitrogen and steam. The temperature must be carefully watched, and not be allowed to rise so high as to occasion the production of white vapours in the retort, as the decomposition is then apt to occur with explosive violence. The reaction may be explained as follows:—Ammonia is a compound of nitrogen with hydrogen. When the nitrate of ammonia is heated, the hydrogen of the ammonia combines with part of the oxygen of the nitric acid, forming water, whilst the nitrogen of the ammonia at the same time becomes oxidized at the expense of another part of the oxygen of the nitric acid. The result is that the whole of the nitrogen, both of the nitric acid and of the ammonia, is liberated in the form of protoxide of nitrogen : thus,



An ounce of the salt furnishes about 500 cubic inches of the gas.

*Properties.*—Protoxide of nitrogen is a transparent, colourless gas, with a faint 'sweetish' smell and taste; it is soluble in about three-fourths of its bulk of cold water. Owing to this circumstance, it should be collected over warm water, which dissolves it much less freely. Under a pressure of 50 atmospheres at  $45^\circ$ , it is reducible to a colourless liquid, which may be frozen into a transparent solid about  $-150^\circ \text{F}$ . (Faraday). When the liquid protoxide is mixed with bisulphide of carbon and exposed to evaporation in vacuo, M. Natterer obtained a reduction of temperature which he estimated at  $-220^\circ \text{F}$ .; this is a lower point than has hitherto been attained by any other means. The gaseous protoxide of nitrogen has a specific gravity of 1.527, which coincides with that of carbonic acid. This gas possesses the qualities neither of an acid nor of an alkali. It supports the combustion of many bodies with a brilliancy resembling that which they exhibit in oxygen. It is, however, at once distinguished from oxygen by its considerable solubility in water. A glowing match bursts into flame when plunged into the protoxide: sulphur burns in it with a pale rose-coloured flame.

Soon after the discovery of the protoxide of nitrogen, Sir H. Davy ascertained that it may be respired for a few minutes: it

then produces a singular species of transient intoxication, attended in many instances with an irresistible propensity to muscular exertion, and often to uncontrollable laughter; hence the gas has acquired the popular name of *laughing-gas*. Different individuals are affected in different degrees and in various ways, according to the temperament of each. In plethoric persons, where there is any tendency to over active circulation through the brain, the experiment is not a safe one. The intoxicating effects pass off in a few minutes, and frequently no recollection of what has passed is retained, and no lassitude is perceived after the extreme exertion. When the gas is to be respired, great attention to its purity is requisite; the nitrate of ammonia from which it is prepared must be perfectly free from hydrochloric acid, as otherwise a little chlorine might be liberated, which, if breathed, would be highly irritating to the lungs.

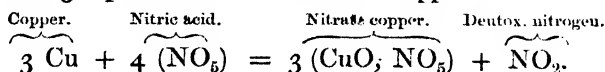
*Composition.*—If protoxide of nitrogen be passed repeatedly through a porcelain tube heated to bright redness, the gas is decomposed into a mixture of oxygen and nitrogen, 2 volumes become expanded permanently into the space of 3 volumes. An easy method of analysing the protoxide of nitrogen consists in mixing it with hydrogen, and passing an electric spark through the mixture. If 4 measures of protoxide of nitrogen be mixed with an excess of hydrogen gas, say with 6 measures of hydrogen, in the bent eudiometer, fig. 239, 10 measures of mixed gas will be produced; and on transmitting the electric spark, inflammation will occur; steam will be formed by the oxidation of the hydrogen, and will immediately condense; the 10 measures will thus be reduced to 6: but the quantity of oxygen contained in the protoxide of nitrogen cannot be at once inferred from this change of bulk: before this can be done it is needful to ascertain how much hydrogen is left in the mixture. This may be effected by mixing the 6 remaining measures with 2 measures of oxygen, thus making 8 measures, and again transmitting the electric spark. Steam will again be formed, and will immediately condense, the 8 measures of the mixture will now be reduced to 5: 3 measures of the gas will therefore have disappeared, two-thirds of which, or 2 measures, are hydrogen: 1 measure of the the gas now left must consequently be oxygen which was added in excess, and the remaining 4 volumes are nitrogen. Of the 6 measures of hydrogen originally added, 4 have therefore combined with oxygen derived from the protoxide; and since 4 measures of hydrogen require 2 measures of oxygen for conversion into water, the 4 measures of the protoxide must have contained 2 measures of oxygen. It appears, also, that protoxide of nitrogen contains its own bulk of nitrogen; since the 4 measures of the gas originally employed furnish

4 measures of nitrogen; this <sup>6</sup>nitrogen is moreover so combined with 2 measures of oxygen, that the 6 measures of the two gases when united have condensed into the space of 4 measures, or into two-thirds of the bulk which they occupied when separate. The specific gravity of the gas shows that this conclusion is correct:—

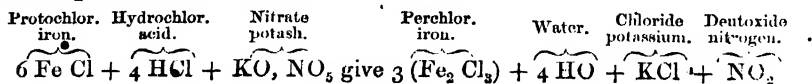
	grains.
For 100 cubic inches of nitrogen weigh . . .	30.12
50 cubic inches of oxygen . . .	17.10
<hr/>	
They give 100 cubic inches of protoxide of nitro- } gen, and weigh . . . . . }	47.22

The proportion of nitrogen contained in the gas may also be ascertained by means of potassium: for if potassium be heated in protoxide of nitrogen, it burns vividly, and is converted into potash, leaving a volume of nitrogen equal to that of the gas employed.

(307) DEUTOXIDE OF NITROGEN: *Binoxide of Nitrogen, or Nitric Oxide*, ( $\text{N}_2\text{O}_2$ ); *Eq.* 30; *Sp. Gr.* 1.039; *Combining Volume*, 4.—If nitric acid be diluted with twice its bulk of water, so as to reduce it to a specific gravity of about 1.2, and be poured upon copper clippings or metallic mercury placed in a retort, brisk action speedily occurs; a gentle heat, if necessary, may be applied until it commences; the retort becomes filled with red fumes, and a gas is disengaged, which if collected over water will be found to be colourless. During this decomposition, 1 equivalent of nitric acid loses 3 equivalents of oxygen, and gives off 1 equivalent of deutoxide of nitrogen, the metal taking oxygen from one portion of the acid, and forming an oxide which dissolves in a portion of the undecomposed acid. The following equation shows the reaction which occurs between 3 equivalents of copper and 4 of nitric acid, resulting in the formation of 1 equivalent of deutoxide of nitrogen, and 3 equivalents of nitrate of copper:—



The deutoxide may also be obtained perfectly pure by digesting hydrochloric acid with iron filings till it will dissolve no more, decanting the clear liquid, and adding to it its own bulk of hydrochloric acid: on placing the solution in a retort, and adding nitrate of potash, the deutoxide of nitrogen is immediately evolved in large quantity. The reaction is not so simple as in the preceding case; it is represented as follows:—



The gas has a strong disagreeable odour, and cannot be respired. The deutoxide of nitrogen has hitherto resisted all attempts to liquefy it. Water does not dissolve more than  $\frac{1}{60}$ th of its bulk. Many burning bodies, such, for instance, as a lighted taper, or phosphorus just kindled, are extinguished when plunged into the gas; but a decomposition of the gas will be effected if the phosphorus be burning vigorously, and it will deflagrate with a brilliancy equal to that produced by its combustion in oxygen. The composition of the deutoxide cannot be ascertained by detonation with hydrogen; for equal volumes of hydrogen and of the deutoxide burn quietly with a green flame on the approach of a light. Gay Lussac analysed the deutoxide of nitrogen by heating charcoal strongly in it; 4 volumes of the gas by this treatment furnish 2 volumes of nitrogen, and 2 volumes of carbonic acid; but carbonic acid contains its own volume of oxygen; the deutoxide must therefore have consisted of 2 volumes of nitrogen united without condensation with 2 volumes of oxygen. The density of the gas confirms the correctness of this result, for by experiment 100 cubic inches weigh rather more than 32 grains, and by calculation,

50 cubic inches of oxygen weigh . . .	17.10
50 cubic inches of nitrogen . . .	15.06
100 cubic inches of binoxide of nitrogen ..	<u>32.16</u>

Potassium burns when heated in the gas, potash being produced. If the experiment be conducted in such a manner as to allow of the residual gas being measured after the combustion is over, 4 volumes of the deutoxide will be found to leave 2 volumes of nitrogen.

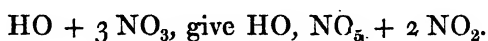
Deutoxide of nitrogen is completely absorbed by a solution of protosulphate of iron, and forms a deep olive-green liquid. All the proto-salts of iron exert a similar action, and according to Peligot, 4 equivalents of the salt of iron absorb 1 equivalent of the deutoxide,  $4(\text{FeO}, \text{SO}_3) + \text{NO}_2$ . The deep colour of the liquid thus formed is employed, as has already been mentioned (305), for the purpose of ascertaining the presence of nitric acid in solution. This green liquid rapidly absorbs oxygen from the air or from gaseous mixtures; when heated, most of the deutoxide is expelled from it unchanged. Solutions of the proto-salts of tin and of mercury also absorb the deutoxide of nitrogen, but they undergo change, and the gas cannot again be expelled from them by heat. Nitric acid also rapidly absorbs the gas. If the acid be concentrated, the solution becomes reddish brown; if more diluted, it is green; if still



weaker, the solution is blue, and if diluted below a specific gravity of 1.15, little of the gas is absorbed and the acid remains colourless.

The deutoxide of nitrogen is neither acid nor alkaline in its characters. It has, however, a very powerful affinity for oxygen, and to this circumstance is owing one of the most characteristic properties of the gas. When mixed with oxygen, or with any gas containing uncombined oxygen, dense red fumes are produced. These red fumes are freely soluble in water, and furnish an acid liquid. Formerly this circumstance was employed to determine the quantity of oxygen in mixture with other gases; but the method is now abandoned, as the absorption is not uniform, owing to the formation in uncertain quantity of a mixture of several soluble oxides of nitrogen. It may, however, be used with advantage as a qualitative test to demonstrate the existence of uncombined oxygen in a gaseous mixture.

(308) NITROUS ACID: *Hyponitrous Acid*, ( $\text{NO}_2$ ); *Equiv. 16*, 38. — By mixing in an exhausted flask 4 volumes of deutoxide of nitrogen with 1 volume of oxygen, both in a perfectly dry state, brownish-red fumes form, which at a cold of  $0^\circ \text{F}$ . condense to a blue very volatile liquid; water immediately decomposes it into nitric acid and deutoxide of nitrogen. The presence of a small quantity of water converts the blue into a dark green liquid, but a larger quantity decomposes it with effervescence: nitric acid is formed, and deutoxide of nitrogen escapes. This reaction may be thus represented:—



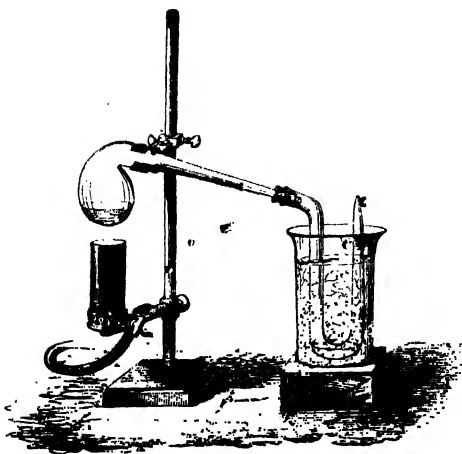
Though in its uncombined form nitrous acid is decomposed with such facility, yet it forms permanent compounds with the alkalis. If deutoxide of nitrogen be placed over a solution of caustic potash, and small quantities of oxygen be added, nitrite of potash is produced in the liquid; and if nitre, or nitrate of soda, be heated to redness until the gas which is evolved begins to contain nitrogen, the residue will be found composed chiefly of nitrite of potash, or soda. These nitrites dissolve in alcohol, and may thus be separated from the corresponding nitrates, which are insoluble. If the nitrite either of potash or of soda be dissolved in water, and nitrate of silver be added, a sparingly soluble nitrite of silver precipitates. By dissolving this precipitate in hot water, it is obtained pure in crystals as the liquid cools. When a fragment of nitrite of potash is moistened with a solution of sulphate of copper, it strikes a brilliant green colour, which is quite characteristic. The addition

of acetic acid to a solution of a nitrite decomposes the salt, and the liquid then strikes an olive-green colour on adding a solution of protosulphate of iron.

(309) PEROXIDE OF NITROGEN: *Hyponitric Acid*, (formerly called Nitrous Acid,)  $\text{NO}_4$ , *Eq. 46*.—The red fumes which appear on mixing the deutoxide of nitrogen with atmospheric air consist mainly of this compound:—2 volumes of oxygen and 4 volumes of the deutoxide of nitrogen in combining condense into the space of 4 volumes; hence its specific gravity should be 1.591. Peroxide of nitrogen may be procured in prismatic crystals by passing 4 volumes of the deutoxide and 2 volumes of oxygen, both perfectly dry, into tubes previously dried with scrupulous care, and cooled down by a mixture of ice and salt. (Peligot, *Ann. de Chimie*, III., ii., 61.) These crystals melt at  $16^\circ \text{F}$ .; at the ordinary temperature of the air they form an orange-coloured liquid, which boils at  $71^\circ \text{F}$ ., and produces a deep red vapour. It is remarkable that after this compound has once been melted it does not freeze even at  $0^\circ$ . This substance is decomposed by water with singular facility; the minutest trace of water is sufficient to prevent the formation of the crystalline compound, occasioning in its stead the production of a green liquid, probably  $\text{NO}_3 + \text{NO}_5 + \text{aq}$ , similar to that obtained by the distillation of nitrate of lead. The peroxide of nitrogen was long considered to possess acid properties, and hence was termed nitrous acid. It, however, does not enter into combination with bases, but is immediately decomposed by them into nitric and nitrous acids; 2 equivalents of the peroxide of nitrogen and 2 equivalents of potash yielding 1 equivalent each of nitrate and nitrite of potash,  $2 \text{NO}_4 + 2 \text{KO} = \text{KO}, \text{NO}_5 + \text{KO}, \text{NO}_3$ . Much speculation has been indulged in as to its probable composition. Berzelius latterly was disposed to regard this compound as a combination of nitric acid with deutoxide of nitrogen:  $3 \text{NO}_4$  may be represented as  $(\text{NO}_2, 2 \text{NO}_5)$ .

If nitrate of lead be dried, and heated strongly in a small glass retort, it is decomposed, oxide of lead is formed, and deep red fumes, consisting of a mixture of peroxide of nitrogen and free oxygen, are produced,  $\text{PbO}, \text{NO}_5 = \text{PbO} + \text{O} + \text{NO}_4$ . If the red vapour be passed through a bent tube surrounded by ice and salt, as shown in fig. 250, the peroxide condenses to a greenish liquid, owing to the presence of a little moisture. Towards the latter part of the distillation the anhydrous peroxide comes over, and if the receiver be changed, it may be obtained in crystals, which are the same as those produced by the mixture of dry oxygen and deutoxide of

,Fig. 250.



nitrogen; the minutest trace of moisture, however, converts them into the liquid form. This liquid is colourless at  $0^{\circ}$ ; it becomes yellow at  $14^{\circ}$  F., and at ordinary temperatures is red. It has a specific gravity of 1.451, boils at  $82^{\circ}$ , and freezes at  $-40^{\circ}$  F. It emits a dense red vapour, which becomes deeper in tint as the temperature rises, till at  $100^{\circ}$  it is almost opaque. This vapour has a suffocating

odour. It supports the combustion of a taper, and of many burning bodies. If water be gradually added to the liquid peroxide it passes through various tints, becoming successively orange, yellow, green, blue, and finally colourless, an effervescence being occasioned during the whole time from the escape of deutoxide of nitrogen; finally, nitric acid in abundance is formed in the liquid. The reaction may be traced as follows:  $2\text{HO} + 3\text{NO}_4 = \text{NO}_2 + 2(\text{HO}, \text{NO}_5)$ . The deutoxide of nitrogen, on mixing with the oxygen of the air, reproduces the peroxide of nitrogen as usual. The different tints assumed by the liquid during dilution appear to be owing to the solution of the deutoxide of nitrogen in varying proportion in the nitric acid produced by the decomposition.

(310) The important influence of proportion upon the products of chemical combination is exhibited in a striking light by these compounds of nitrogen with oxygen. The same elements, according to the quantities in which they are united, may, as in nitric acid, produce one of the most corrosive compounds in the range of chemistry; or may give rise, as in the case of the protoxide of nitrogen, to a stimulating and intoxicating gas, which may be breathed with impunity, while the intermediate combinations exhibit properties entirely different from either. A broad distinction may also be easily traced between the results of mixture and those of true chemical union. The properties of the atmosphere are the results of simple admixture; the chemical qualities of oxygen appearing to be simply diluted by its apparently inert companion, nitrogen (just as the sweetness of sugar is reduced by the

addition of water); whilst each one of the true combinations of nitrogen with oxygen exhibits characters sufficiently distinct from those of either of its components.

## § II.—COMPOUNDS OF NITROGEN WITH HYDROGEN.

AMMONIA, ( $\text{H}_3\text{N}$ ); *Eq.* 17; *Sp. Gr.* 0.59; *Combining Volume*, 4.

(311) (*Volatile Alkali, or Hartshorn.*)—This important compound has received the name of ammonia, from the circumstance of its having been obtained from a salt termed sal ammoniac, first procured in Libya, near the temple of Jupiter Ammon. Nitrogen and hydrogen do not combine directly with each other; nevertheless, their indirect combination is a circumstance of continual occurrence. The spontaneous decomposition of most animal matters, which contain both hydrogen and nitrogen, and almost every process of oxidation in the presence of moisture, is attended with the formation of ammonia. The hydrogen, at the moment of its liberation from the water by deoxidation, appears to enter into combination with the nitrogen of the atmosphere; which, to a small extent, is held in solution, and thus ammonia is formed. Moistened iron filings, if exposed to the air, become rusty, and the oxidized compound retains a small quantity of ammonia. The deoxidation of dilute nitric acid by the metals, also frequently gives rise to the production of ammonia; both nitrogen and hydrogen are liberated simultaneously, a part of the water undergoing deoxidation at the same time that the acid is decomposed. Tin, zinc, and iron, exhibit this effect in a marked degree.

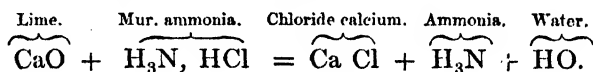
Mr. Nesbit (*Q. J. Chem. Soc.*, 12, 281) has proposed to use this reaction as a means of estimating the quantity of nitric acid in solutions; for he finds that by dissolving zinc very slowly in dilute hydrochloric acid, and adding the nitric solution in small quantities at a time, the whole of the nitric acid is converted into ammonia.

Ammonia exists in minute quantity in the atmosphere.\* It is

\* According to the elaborate researches of M. Ville, which appear to have been conducted with every precaution to ensure accuracy, 10,000,000,000 parts of air contained on the average, in the year 1851, 237 parts by weight of ammonia, and in 1852, 210 parts. This amounts to about 1 volume of ammonia in 28,000,000 of air: other experimenters make the quantity considerably higher. The proportion of ammonia contained in rain water is liable to considerable variation: in 1,000,000 parts of rain water collected in Paris during the last five months of 1851, M. Barral found 3.49 parts; Boussingault, at Liebfraumburg, in 1852, found only 0.744 parts; and Messrs. Lawes and Gilbert at Rothamsted, in 1853 and 1854, found the average amount from March to August to be 1.142, from September to February, 0.927 parts: the average of the two last determinations would give about 1 grain of ammonia in 14 gallons of rain water.

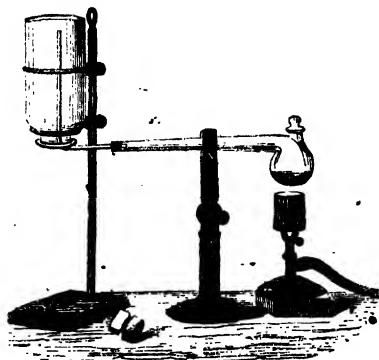
also found in clayey and in peaty soils, both of which absorb it freely. For the purposes of manufacture it is, however, always procured by the distillation, in closed vessels, of organic matters containing nitrogen. The principal part of the ammonia used in this country is obtained from the refuse products of the distillation of coal for the manufacture of gas. Amongst these products is a considerable quantity of carbonate and hydrosulphate of ammonia, which dissolve in water and form the ammoniacal liquor of the gas works; this liquor is saturated with sulphuric or with hydrochloric acid, and thus the sulphate or muriate of ammonia of commerce is procured.

If equal weights of quicklime and either of the salts last named be separately powdered and intimately mixed, the powder, on being transferred to a retort and gently heated, gives off abundance of pure ammonia, as a transparent colourless gas, of the peculiar pungent odour of smelling salts. The lime combines with the acid and sets the ammonia at liberty: thus,



*Properties.*—Ammonia produces a flow of tears from the eyes; it has an acrid taste, and, when breathed in a concentrated form, is fatal to life, from its irritating effects on the lungs. In a more diluted form it is a highly valuable stimulant. Ammonia does not support the flame of burning bodies, but is feebly combustible; a jet of the gas directed across the stream of hot air issuing from a lighted argand lamp, burns with a very pale green flame. Ammonia is extremely soluble in water, and must therefore be collected either over mercury or

FIG. 251.



by displacement, in the manner shown in fig. 251. The latter mode of collecting it may easily be effected, as the gas has little more than half the density of atmospheric air, its sp. gr. being only 0.59. Ammonia has a powerful alkaline reaction, and turns turmeric paper brown. When collected by displacement, the gas must be allowed to pass into the bottle until a piece of dry turmeric paper held to the

mouth of the bottle is immediately turned brown; the tube

is then withdrawn, and the stopper, slightly greased, is inserted. Ammonia neutralizes the most powerful acids, and forms a very important class of salts. Any volatile or gaseous acid brought into an atmosphere containing ammonia, produces a white cloud, from the formation of a solid salt. This property is often employed to detect small quantities of ammonia. Quicklime or potash is mixed with the solution suspected to contain ammonia, and the whole gently warmed in a tube. A rod moistened with hydrochloric acid diluted with half its bulk of water, is placed in the upper part of the tube or vessel, and if ammonia be present, white fumes appear, even when the quantity of ammonia is too small to be distinguished by the smell.

*Composition.*—The composition of ammonia may be ascertained as follows. If the dry gas be passed slowly through a porcelain tube containing iron turnings or spongy platinum, heated to bright redness, the gas is decomposed; it becomes dilated to double its volume; 4 volumes of ammonia become 8; and the gas produced is found to consist of a mixture of 2 volumes of nitrogen with 6 volumes of hydrogen. A portion of this mixture may be detonated with oxygen. If 8 measures be mixed in the bent eudiometer with 4 of oxygen, so as to make 12 measures in the whole, 3 measures will be left, after the transmission of the electric spark, owing to the formation of steam and its subsequent condensation. One-third of the volume of gas which has disappeared, or 3 measures, will be oxygen, and two-thirds, or 6 measures, will be hydrogen. No carbonic acid has been formed, for the residual gas is not altered in bulk by agitation with potash: by mixing the remaining 3 volumes with their own bulk of hydrogen and again transmitting the electric spark, 1 measure out of the 3 may be proved to consist of oxygen added in excess; therefore the remaining 2 of nitrogen were present in the ammonia in combination with the 6 of hydrogen which have condensed as steam; consequently the 4 volumes of ammonia must have been formed by 6 volumes of hydrogen, and 2 of nitrogen, condensed into half their bulk.

Other striking proofs of the composition of ammonia are afforded by the action of heat upon some of its salts. The decomposition of nitrate of ammonia offers one of these. By the action of heat, as already explained (306), the nitrate of ammonia ( $\text{H}_3\text{N} \cdot \text{HO}, \text{NO}_3$ ) is decomposed into water and protoxide of nitrogen,  $4 \text{HO} + 2 \text{NO}$ , the 3 equivalents of hydrogen in the ammonia combine with 3 equivalents of oxygen in the nitric acid, and leave the nitrogen of the ammonia to combine with deutoxide of nitrogen derived from the nitric acid.  $\text{NO}_2\text{O}_3 + \text{H}_3\text{N} = (\text{NO}_2 + \text{N}) \text{ (or } 2 \text{NO)} + 3 \text{HO}$ .

If a solution of the nitrite of ammonia ( $\text{H}_3\text{N}$ ,  $\text{HO}$ ,  $\text{NO}_2$ ) be heated, the salt is decomposed, water and pure nitrogen are liberated. The result may be thus represented:  $(\text{H}_3\text{N}, \text{HO}, \text{NO}_2) = 4\text{HO} + 2\text{N}$ : the hydrogen of the ammonia is in this case exactly sufficient to combine with the oxygen of the nitrous acid, forming water: this is an excellent mode of obtaining pure nitrogen.

Ammoniacal gas may be liquefied by exposure to a cold of  $-40^\circ\text{F}$ ., or still more readily by generating it under the pressure of its own atmosphere. The easiest method is the following:—Chloride of silver in powder is exposed to a current of dry ammoniacal gas; the ammonia is rapidly absorbed, and the chloride increases in weight more than one-third. This substance is placed in one limb of a strong tube (182), bent to an obtuse angle, and then hermetically sealed; on applying heat to the chloride, and cooling the other end of the tube with a freezing mixture, the ammonia condenses as a colourless liquid, which exerts a pressure of 6.9 atmospheres at  $60^\circ$ , and has a specific gravity of 0.731. By a cold of  $-103^\circ\text{F}$ ., it is frozen to a white translucent crystalline solid, which is denser than the liquid (Faraday). The chloride of silver reabsorbs the liquefied ammonia, and slowly reproduces the original compound.

*Solution of Ammonia.*—A solution of ammonia in water is a reagent in continual requisition. When ammoniacal gas is passed into water it is rapidly absorbed, with considerable extrication of heat; at a temperature of  $50^\circ\text{F}$ ., water takes up about 670 times its volume of the gas, increasing in bulk nearly one half, and becoming specifically lighter; this saturated solution has a density of 0.875 (Davy). Such a solution contains nearly one-third of its weight of ammonia. The following table indicates the strength of solutions of pure ammonia of different specific gravities, according to the experiments of Sir H. Davy:—

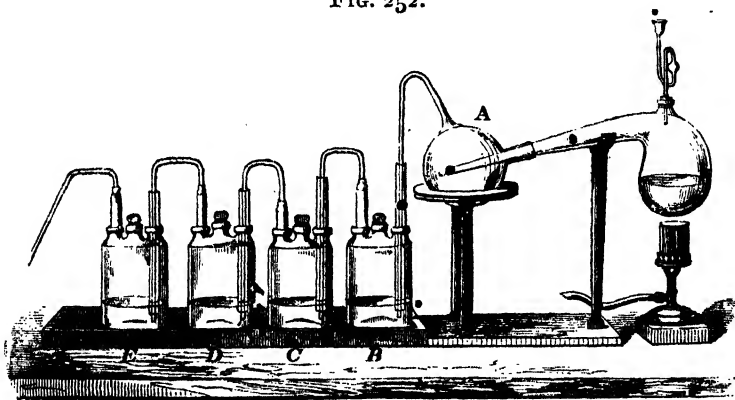
Specific gravity.	Ammonia in 100 parts by weight.	Specific gravity.	Ammonia in 100 parts by weight.
0.8750	32.50	0.9435	24.53
0.8875	29.25	0.9476	13.46
0.9000	26.00	0.9513	12.40
0.9054	25.37	0.9545	11.56
0.9166	22.07	0.9573	10.82
0.9255	19.54	0.9597	10.17
0.9326	17.52	0.9619	9.60
0.9385	15.88	0.9692	9.50

Solution of ammonia is colourless and intensely alkaline; it has an acrid caustic taste, and blisters the skin if applied to it in a con-

centrated form; it freezes at about  $-40^{\circ}$  F. Simple exposure to the air is attended with an escape of the gas, which occasions the pungent smell of the liquid. By heat the ammonia is rapidly expelled with the appearance of ebullition, thereby furnishing a ready extempore method of procuring the gas. By boiling the liquid for some time, the whole of the ammonia may be expelled, so that nothing but water is left in the retort.

Solution of ammonia is prepared on the large scale by mixing together in a capacious retort equal weights of well-burned quicklime and sal ammoniac; the lime is slaked and made into a paste with water before mixture. The retort is then connected with a series of bottles similar to those used for condensing nitric acid. If the operation be conducted on the small scale in the laboratory, the arrangement shown in fig. 252 may be adopted. The three-necked bottles, B, C, D, E, are known by the name of Woulfe's

FIG. 252.



bottles; in the globe, A, a small quantity of water is placed, to retain any solid particles which may be mechanically carried over by the gas; in the first bottle, B (which may be kept cool by immersion in cold water), a quantity of water equal in weight to that of the sal ammoniac used is introduced, taking care that it shall not fill more than half the capacity of the bottle; whilst the second contains water to condense any gas that may escape through the first. Each bottle is provided with a safety tube open at both ends, so that if the gas were absorbed in B, for example, more rapidly than it was supplied, instead of the liquid being driven back from bottle C, air would enter by the safety tube, and the equilibrium would be restored. The tube which delivers the gas passes down through the safety tube and projects a little beyond its lower



opening, so that the gas rises in bubbles through the liquid, and collects in the bottle; an air-tight joint which can be mounted and dismounted immediately is thus obtained.

Solution of ammonia, if pure, should, when evaporated, leave no solid residue; the presence of carbonic acid may be detected by lime water, which it renders milky; that of chlorine by neutralizing with pure nitric acid, and adding nitrate of silver, when it gives a white cloud; that of sulphuric acid by a white precipitate with nitrate of baryta after dilution and saturation with nitric acid; that of lime by a white precipitate on adding oxalate of ammonia; and that of copper or lead derived from the apparatus, by a black or brown precipitate or cloud with sulphuretted hydrogen. Lead in small quantity is a very frequent impurity in the commercial solution; it is derived from the action of the ammonia on the flint-glass bottles in which it is often improperly kept.

Alcohol also dissolves ammonia in abundance. The salts of ammonia will be described with those of the other alkalis.

(312) AMIDOGEN, ( $H_2N$ ); *Equivalent*, 16.—Ammonia is the only compound of hydrogen and nitrogen that has been obtained in the isolated form. When, however, potassium is heated gently in perfectly dry ammoxiacal gas, the ammonia disappears, half its volume of hydrogen is produced, and a fusible olive-green compound is formed, consisting of  $K, H_2N$ . The ammonia is decomposed by the potassium in the following manner:  $H_3N + K$  becomes  $KH_2N + H$ . The compound  $H_2N$  has received the name of amidogen, and it appears capable of existing in combination with several metals, and with a variety of bodies derived from the organic kingdom. This class of compounds has received the name of *amides*; they will be more conveniently examined hereafter.

AMMONIUM, ( $H_4N$ ); *Equivalent*, 18.—This compound, like the one just mentioned, has not been obtained in a separate form. All the usual salts of ammonia, however, appear to contain it. Nitrate of ammonia, for example, consists not simply of  $H_3N, NO_5$ , but in addition contains an equivalent of water which cannot be expelled by heat without the entire decomposition of the salt; this nitrate is therefore looked upon as a nitrate of oxide of ammonium,  $H_4NO, NO_5$ . Sal ammoniac is on this view regarded as chloride of ammonium,  $H_4N, Cl$ . The full discussion of the grounds upon which this theory rests will be best postponed till we enter upon a description of the salts of ammonia.

## CHAPTER VI.

## THE HALOGENS.

BEFORE proceeding to notice some other compounds of the four elements already described, it will be desirable to examine the other non-metallic simple substances. We pass on therefore to a group of four closely allied bodies, viz., chlorine, bromine, iodine, and fluorine. These elements are characterised by the powerful activity of their affinities for other substances at the ordinary temperature of the air, and consequently none of them are found in an uncombined state.

## § I. CHLORINE.

*Symbol*, Cl; *Equivalent*, 35.5; *Specific Gravity*, 2.47;  
*Combining Volume*, 2.

(313) Chlorine, the most important of the group, is abundantly met with in combination with sodium, with which it constitutes ordinary table salt. This necessary of life occurs plentifully in beds in various parts of the world, and is the most abundant of the saline bodies contained in the waters of the ocean.

*Properties*.—Chlorine is a transparent gas of a greenish-yellow colour (whence the name is derived, from *χλωρος*, 'green'), and of a powerful suffocating odour, producing, if breathed, even when largely diluted with air, distressing irritation of the air passages, attended with coughing. It is much heavier than air, having a specific gravity of 2.47, according to the experiments of Gay Lussac and Thénard; 100 cubic inches weigh between 77 and 78 grains. Under a pressure of 4 atmospheres at 60°, it condenses to a yellow limpid liquid, of specific gravity 1.33, and which remains unfrozen even at the cold of —220° F. Chlorine is soluble in about half its bulk of cold water; this solution, which is readily formed by agitating the gas and water together, has the colour, odour, and taste of the gas. Chlorine, in consequence of this solubility, cannot be advantageously collected over cold water; water at 100° absorbs it much less freely. Mercury is acted upon by the gas with great rapidity. It is necessary, therefore, either to use warm water in the pneumatic trough, or to receive it by the process of displacement in dry bottles. With water, chlorine forms a definite *hydrate*

(Cl + 10 Aq), which crystallizes at  $32^{\circ}$ ; if it be enclosed in hermetically sealed tubes it furnishes a ready method of obtaining liquefied chlorine, as by a gentle heat it is easily decomposed into water and free chlorine.

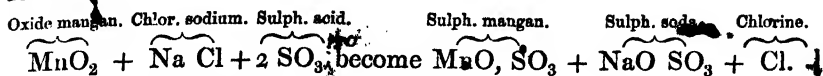
Chlorine is not combustible, and it does not combine directly with oxygen. A taper burns in it with a reddish smoky flame, the hydrogen of the combustible vapour of the wax combining with the chlorine, whilst part of the carbon, for which its affinity is but small, is deposited. Many bodies, however, take fire spontaneously when introduced into chlorine; this is the case with phosphorus; many of the metals in a finely divided state do the same; copper leaf, finely powdered antimony, and arsenic, are among the number. A great number of organic substances rich in hydrogen are decomposed by chlorine, sometimes with such rapidity as to inflame them; a bit of paper dipped into oil of turpentine and plunged into the gas bursts into flame, and deposits an abundance of a black carbonaceous compound.

The action of chlorine upon bodies containing hydrogen is often of a very peculiar kind. It combines with part of the hydrogen and withdraws it from the combination; each equivalent of hydrogen unites with an equivalent of chlorine, forming a powerful acid, the hydrochloric, (H Cl); but at the same time for each equivalent of hydrogen so withdrawn from the original compound, an equivalent of chlorine is substituted. It is in this way that chlorine exerts those bleaching powers which have rendered so essential a service to the calico-printer and the paper-maker. Most of the vegetable colouring matters contain hydrogen, and are decomposed by chlorine, whilst colourless or nearly colourless compounds containing chlorine are formed, instead of the coloured compounds with hydrogen. If a solution of chlorine be mixed with some of the blue liquid formed by dissolving indigo in sulphuric acid, or with ordinary writing ink, or with tincture of litmus, the colour will in each case be immediately and almost completely discharged, and it cannot be subsequently restored.

Another property of chlorine of great value is its disinfecting power, by which is meant its power of destroying noxious vapours and miasmata; with this view it is frequently employed for fumigating buildings after the occurrence of contagious diseases.

*Preparation.*—Chlorine may be easily prepared from a mixture of 7 parts by weight of oil of vitriol, previously diluted with 7 parts of water, and allowed to cool, and 4 parts of pounded chloride of sodium intimately mixed with 3 parts of finely pulverized, black

oxide of manganese. The decomposition may be represented as follows:—



The gas comes off slowly in the cold, but freely on the application of a gentle heat. A little hydrochloric acid is always formed in the reaction; this acid is easily removed from the chlorine by allowing the gas to bubble up through a vessel containing water, in the manner shown in fig. 245, where a similar apparatus is employed for carbonic oxide.

The manufacture of chlorine is practised on an enormous scale in the preparation of bleaching powder, or chloride of lime. It is generally prepared in capacious stills, sufficiently large to hold 200 gallons of liquid; these are frequently made of Yorkshire flags clamped together with iron work, and the joints rendered tight by vulcanized caoutchouc. A leaden still, shown in section at *a*, fig. 253, may be employed for the same purpose. The lower part of these stills is enclosed in a case, *dd*, through which a current of steam is admitted by the pipe *d*. Hydrochloric acid in solution, of specific gravity from 1.160 to 1.170 (which is obtained as a waste product in the manufacture of carbonate of soda from sea salt), is run through the curved funnel, *b*, into the stills, which are charged at the opening, *f*, with oxide of manganese in small lumps. Chloride of manganese is formed, and free chlorine is liberated in abundance, and escapes through the pipe, *a*; when the charge is exhausted it is withdrawn by the pipe, *g*: the materials are agitated from time to time by means of the stirrer, shown at *c c*. The different parts of the apparatus are rendered tight, and at the same time admit of being rapidly mounted or disconnected by the employment of 'water-joints,' the pipes drop into small gutters, as shown at *a*, at *e e*, and at *f*, filled with sulphuric acid, which effectually prevents the escape of the gas. The reaction is illustrated in the following symbols:

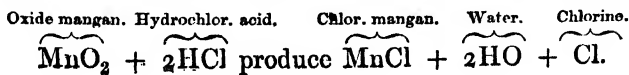
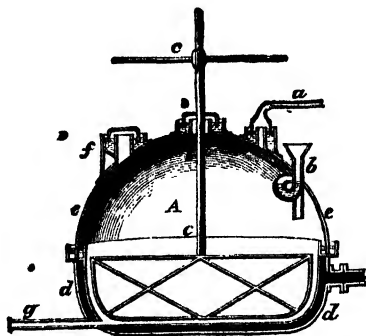


FIG. 253.



This process may also often be resorted to on the small scale in the laboratory with advantage. Three ounces of powdered oxide of manganese with half a pint of the commercial muriatic acid diluted with 3 ounces of water, will yield between 3 and 4 gallons of the gas. Care must be taken not to use an acid more dilute than 1:15 in the preparation of the gas; since, owing to a neglect of this precaution, explosions have in some instances occurred in operating on the large scale. Hypochlorous acid, or one of the lower explosive oxides of chlorine, was probably formed in these cases.

*Chlorides.*—Chlorine combines with all the non-metallic elements, and forms with many of them compounds of great importance; it also enters into combination with all the metals, and it combines directly with a large number of them, with the usual phenomena of combustion; the compounds which it forms are termed *chlorides*. With the exception of the chloride of silver and the sub-chlorides of mercury and copper, they are all more or less soluble in water. It frequently happens that chlorine combines with the same metal in more proportions than one: for example, with iron a protochloride ( $\text{FeCl}$ ) and a sesquichloride ( $\text{Fe}_2\text{Cl}_3$ ) may be formed; with platinum a protochloride ( $\text{PtCl}$ ) and a bichloride ( $\text{PtCl}_2$ ) may be obtained; and generally, for each oxide of the metal which is capable of uniting with acids to form salts, a corresponding chloride exists. The chlorides of the metals are usually solid, but a few, as the bichloride of tin ( $\text{SnCl}_2$ ), and that of titanium ( $\text{TiCl}_2$ ), the trichloride of arsenic ( $\text{AsCl}_3$ ), and the pentachloride of antimony ( $\text{SbCl}_5$ ), are liquid at the ordinary temperature; the perchloride of manganese ( $\text{Mn}_2\text{Cl}_7$ ) is gaseous. All the metallic chlorides fuse at a heat attained without difficulty, many of them being partially volatilized in the operation; and the chlorides of gold, platinum, palladium, and iridium are decomposed by ignition, the metals remaining in the uncombined form. The chlorides of the other metals are not decomposed by heat. All the chlorides, when heated with black oxide of manganese and sulphuric acid, evolve chlorine gas.

In many cases chlorine unites with the oxides of the metals. If the oxide of the metal be soluble in water, the *oxychloride* which is formed is soluble likewise, and the compound is remarkable for its bleaching properties. Chloride of lime ( $\text{CaOCl}$ ), and chloride of potash ( $\text{KOC}$ ), are instances of this kind. Sometimes the chloride of a metal combines with its oxide and forms an insoluble oxychloride, as is the case with the oxychloride of mercury ( $\text{HgO} + \text{HgCl}$ ). It is a still more frequent occurrence that a

chloride of one of the alkaline metals combines with a chloride of one of those metals which have a feebler attraction for oxygen, and the oxides of which partake rather of the character of acids than of bases. Thus we have a double chloride of platinum and potassium ( $\text{KCl}$ ,  $\text{PtCl}_2$ ), and double chloride of gold and sodium ( $\text{NaCl}$ ,  $\text{AuCl}_3 + 4 \text{ aq.}$ ).

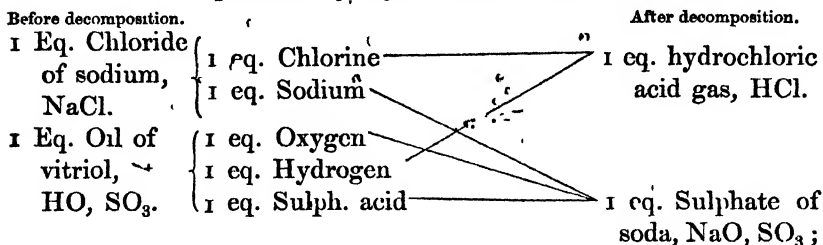
Chlorine when in solution in the uncombined form is easily recognised by its odour and its bleaching properties. Both when free, and when combined with a metal, it gives, on the addition of a solution of nitrate of silver, a curdy, flocculent, white precipitate, which changes to violet on exposure to light: this white precipitate consists of chloride of silver, and is easily re-dissolved by adding a small quantity of solution of ammonia, but it is insoluble in nitric acid. Sub-nitrate of mercury also gives a white precipitate of sub-chloride of mercury in solutions of the metallic chlorides; the calomel ( $\text{Hg}_2\text{Cl}$ ) thus formed is insoluble in nitric acid, and is instantly blackened by the addition of a few drops of ammonia.

(314) HYDROCHLORIC ACID: *Muriatic Acid*, ( $\text{HCl}$ ); *Equivalent*, 36.5; *Specific Gravity*, 1.2474; *Combining Volume*, 4.—The most important of the compounds which chlorine forms with the non-metallic elements is obtained by its combination with hydrogen. The two gases may be mixed in equal volumes, and they will remain without action upon each other, if kept in the dark; but the moment they are brought into direct sun-light they unite with a powerful explosion, and a colourless intensely acid gas is the product. In diffused daylight the combination takes place gradually; but the application of a lighted match, or the passage of the electric spark through the mixture, instantly determines its explosion. Two volumes of chlorine unite thus with 2 volumes of hydrogen, producing 4 volumes of hydrochloric acid; no condensation therefore occurs in the act of union. So powerful is the affinity of chlorine for hydrogen, that if a solution of chlorine in water, or if the gas itself, in a moist state, be exposed to the sun's rays, in either case water is decomposed, hydrochloric acid is formed, and the oxygen of the water is liberated: in the dark, however, chlorine has no power to decompose water.

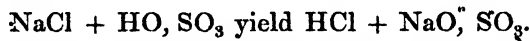
Hydrochloric acid gas is easily procured by placing fragments of common salt (which has been fused in a crucible at a red heat and allowed to cool,) in a glass retort, and pouring over it twice its weight of oil of vitriol. Abundance of hydrochloric acid gas escapes; it must be collected either over mercury or by displacement of the air

from dry bottles. In this case the water of the oil of vitriol yields hydrogen to the chlorine of the common salt, whilst the oxygen combines with the sodium and forms soda, which unites with the sulphuric acid to form sulphate of soda, as is shown in the following diagram:—

*Preparation of Hydrochloric Acid Gas.*



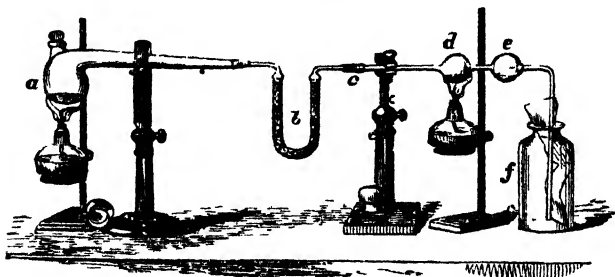
or simply thus,



The composition of hydrochloric acid may be analytically determined by heating sodium in a measured volume of the gas. The metal burns vividly, and liberates a quantity of hydrogen equal in bulk to that of half the gas employed; common salt is formed at the same time.

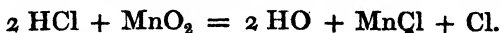
The presence both of hydrogen and of chlorine in the acid gas is easily shown by the following experiment (Graham):—A quantity of hydrochloric acid is liberated from fused chloride of sodium by oil of vitriol, contained in the retort, *a*, fig. 254, and is dried by

FIG. 254.



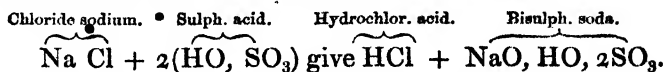
being passed through a tube, *b*, filled with chloride of calcium; this tube is connected by vulcanized caoutchouc, *c*, with a tube upon which two bulbs have been blown; in the first of these, *d*, some pounded anhydrous black oxide of manganese is placed: a piece of litmus paper inserted in the bottle, *f*, which receives the escaping gas, is quickly reddened. On applying heat to the bulb, *d*, con-

taining the oxide, chloride of manganese is produced, and not being volatile it remains in the bulb, whilst water begins to form and condenses in the second bulb, *e*, and in the meantime free chlorine passes on into the bottle, *f*, showing itself by its peculiar colour and its bleaching effect upon the litmus paper. The reaction has already been explained, and may be represented by the following symbols:



*Properties.*—Hydrochloric acid is a colourless gas of a peculiar pungent odour, and an intensely acid taste; it irritates the eyes, and if breathed when diluted produces coughing. It is heavier than air, and has a specific gravity of 1.2474; 100 cubic inches weigh 39.64 grains. Under a pressure of 40 atmospheres at 50° F. it condenses to a colourless liquid of sp. gr. 1.27, which dissolves bitumen, and which has never been frozen. Hydrochloric acid gas is incombustible, and extinguishes burning bodies. It reddens dry litmus paper; when allowed to escape into the air it produces white fumes by condensing the atmospheric moisture, and forming with it a body less volatile than pure water. It is instantly absorbed by water: a lump of ice liquefies in a jar of the gas and absorbs it in a moment.

(315) *Solution of Hydrochloric Acid.*—The solution of hydrochloric acid in water is an indispensable requisite in the laboratory. It is easily prepared for use by placing in a capacious retort 3 parts of fused chloride of sodium in fragments, and introducing gradually, through a bent funnel, 5 parts of oil of vitriol. The retort is connected with a series of Woulfe's bottles; in the first a small quantity of water is placed to detain any impurities which might be mechanically carried over with the gas; the second bottle may contain 4 parts of water, and should be immersed in a vessel of cold water, as the condensation of the gas is attended with a great disengagement of heat. On applying a gentle heat to the retort the acid comes over and is condensed; an easily soluble bisulphate of soda remains in the retort, and is formed as follows—



For manufacturing purposes the decomposition is effected in iron cylinders, like those employed in the preparation of nitric acid, and only one half the quantity of sulphuric acid prescribed above, is used. The acid in this case is in the proportion of one equivalent to each equivalent of salt, neutral sulphate of soda remaining in the cylinder, whilst the acid is condensed in a series of salt-glazed stoneware jars, arranged as Woulfe's bottles.



Water at  $46^{\circ}$  F. is stated by Sir H. Davy to absorb about 480 times its bulk of hydrochloric acid, increasing in volume about one-third and acquiring a density of 1.2109. It forms a colourless fuming liquid, which, by a slight elevation of temperature, parts with the gas abundantly; at this strength it contains nearly 43 per cent. of acid, being about in the proportion of 1 equivalent of acid to 6 of water ( $\text{HCl} + 6 \text{ aq.}$ ).

If the strong acid is placed in a retort and distilled, it loses hydrochloric acid, until the liquid which remains has a density of 1.100 at  $60^{\circ}$  F.; at this point it distils unchanged. A weaker acid if distilled parts with its water freely, until it acquires the density of 1.100, and then it likewise distils unchanged, at a temperature of  $233^{\circ}$  F. Such an acid contains about 20 per cent. of hydrochloric acid, and consists of 16 equivalents of water and 1 of hydrochloric acid ( $\text{HCl} + 16 \text{ aq.}$ ). Common hydrochloric acid may therefore easily be purified by dilution till it has a sp. gr. of 1.1 and then distilling. This appears to be the only stable hydrate of hydrochloric acid, though M. Bincau, by concentration of the acid, at the ordinary temperature of the air, in vacuo over sulphuric acid, obtained a definite hydrate ( $\text{HCl} + 12 \text{ HO}$ ) of sp. gr. 1.128, containing 25 per cent. of the anhydrous acid. According to this observer (*Ann. de Chimie*, III., vii., 259), the vapour of the acid of sp. gr. 1.10 has a density of 0.69, 1 volume of the acid and 8 volumes of aqueous vapour being united without condensation.

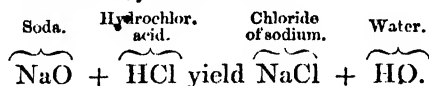
The following table, founded on the experiments of E. Davy, indicates the amount by weight of hydrochloric acid in 100 parts of solution of the acid of the various densities therein enumerated, at a temperature of  $77^{\circ}$  F.

Specific gravity.	Hydrochloric acid in 100 parts.	Specific gravity.	Hydrochloric acid in 100 parts.
1.21	42.43	1.10	20.20
1.20	40.80	1.09	18.18
1.19	38.38	1.08	16.16
1.18	36.36	1.07	14.14
1.17	34.34	1.06	12.12
1.16	32.32	1.05	10.10
1.15	30.30	1.04	8.08
1.14	28.28	1.03	6.06
1.13	26.26	1.02	4.04
1.12	24.24	1.01	2.02
1.11	22.22		

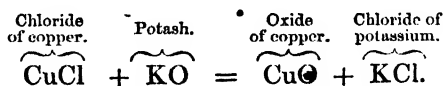
Commercial hydrochloric acid is liable to be contaminated with iron, which gives it a yellow colour; and with the chlorides of

sodium and of arsenic, the latter derived from the sulphuric acid employed in its preparation. Sulphuric and sulphurous acids, and free chlorine are also often present in it. If pure, the acid should leave no residue when evaporated; on saturating it with ammonia it should give no precipitate of oxide of iron: sulphuretted hydrogen should produce no turbidity in it, which would be the case if arsenic, free chlorine, or sulphurous acid were present; and on dilution with three or four times its bulk of water, no white cloud of sulphate of baryta should be produced by the addition of chloride of barium. A solution of hydrochloric acid is decomposed by all the metals which decompose water at a red heat. The metal is dissolved, and hydrogen gas is set free, just as when iron or zinc is acted upon by dilute sulphuric acid: for example,  $\text{HCl} + \text{Zn} = \text{ZnCl} + \text{H}$ .

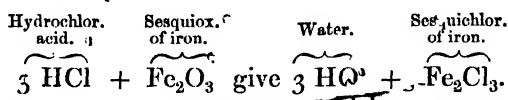
(316) *Action of Hydrochloric Acid on Metallic Oxides.*—The action of hydrochloric acid upon the oxides of the metals is peculiar. Protoxides dissolve in the acid, and appear to combine with it; but on evaporating the liquid, a compound is obtained, in which neither hydrochloric acid nor the metallic oxide is present, and which contains neither hydrogen nor oxygen: when soda ( $\text{NaO}$ ), for example, combines with the hydrochloric acid, the hydrogen of the acid is exactly sufficient by combination with the oxygen of the oxide to form water, which evaporates or remains in the solution, whilst the metal and the chlorine unite directly with each other, as is shown by the following symbols:—



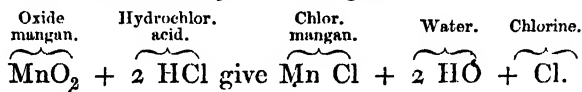
But though the metal may exist in solution in the form of chloride, this circumstance does not prevent its precipitation in the form of oxide, when a strong base, such as potash, is added to a solution which contains the chloride of the metal in question, provided that the metal be capable of forming an oxide insoluble in water. For example, if to a boiling solution of chloride of copper a solution of potash be added, the potassium displaces the copper from the chlorine, and the oxygen with which the potassium was previously combined, is transferred to the copper, whilst the black oxide of copper precipitates. It is, in fact, an ordinary instance of double decomposition:—



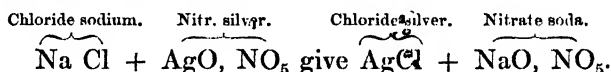
A reaction not less instructive occurs when oxides containing a larger proportion of oxygen than the protoxides are treated with hydrochloric acid. When, for instance, 1 equivalent of sesquioxide of iron ( $\text{Fe}_2\text{O}_3$ ) is subjected to its influence, 3 equivalents of hydrochloric acid are decomposed, 3 equivalents of water are formed, and 1 equivalent of sesquichloride of iron is obtained in solution:—



It sometimes happens that no chloride corresponding to the oxide exists. There is, for example, no bichloride of manganese: in this case one equivalent of the binoxide of manganese decomposes 2 equivalents of hydrochloric acid, 2 equivalents of water and 1 equivalent of protochloride of manganese are formed, whilst the second equivalent of chlorine is liberated; this being in fact the usual mode of obtaining chlorine gas.



The presence of hydrochloric acid, and of the soluble chlorides in solution is indicated by the formation of a white, insoluble, curdy precipitate of chloride of silver, when a solution of nitrate of silver is added to the liquid: for example—



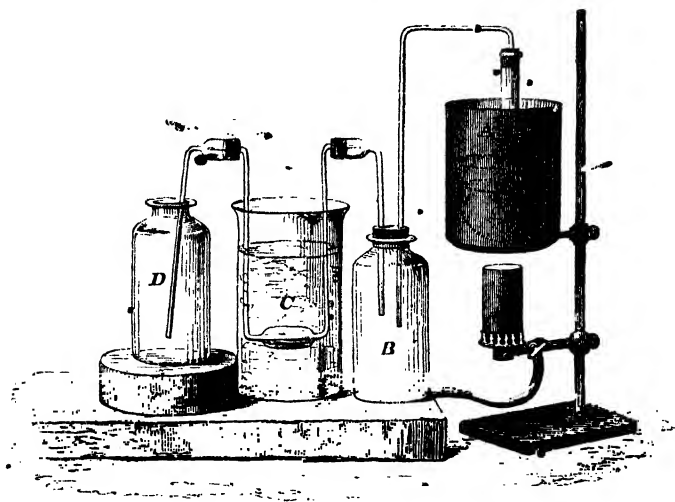
This precipitate is soluble in ammonia, but insoluble in nitric acid.

(317) **AQUA REGIA; Nitro-Muriatic Acid.**—The name of aqua regia was given by the alchemists to a mixture of nitric with hydrochloric acid, from the power that it possesses of dissolving gold, the ‘king of metals.’ Platinum and gold are insoluble in either acid separately; but when the two acids are mixed, they mutually decompose each other; free chlorine, and abundant ruddy fumes, long mistaken for peroxide of nitrogen, being liberated. The chlorine in the moment of its extrication acts upon the metals and dissolves them. The nature of the reaction and the true composition of these fumes, however, has only recently been correctly ascertained by M. Gay Lussac; the investigation formed indeed one of the last scientific labours of this distinguished chemist (*Ann. de Chimie*, III. xxiii. 203).

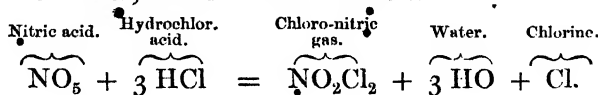
**Chloro-Nitric Gas, ( $\text{NO}_2\text{Cl}_2$ ).**—If a mixture of 1 part of con-

concentrated nitric acid and 3 parts of hydrochloric acid, be placed in a flask and subjected to a gentle heat in the water bath, A, fig. 255, red fumes pass off in abundance. These vapours, if transmitted through a bottle, B, which may be cooled by immersion in melting

FIG. 255.

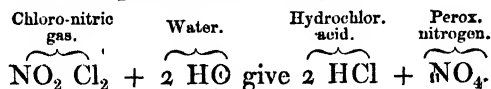


ice, deposit a little volatilized hydrochloric acid and water, but the red fumes pass on, and may be condensed as a heavy red liquid in the tube receiver, C, which is plunged into a mixture of ice and salt, while free chlorine escapes from the open extremity of the tube, C, and appears in the bottle, D. The liquid may be preserved by sealing up the fine tubes on either side by means of the blowpipe. The object of drawing out the extremities of the tube, C, is to protect the corks through which they pass from the corrosive action of the chloro-nitrous vapour. If it be desired to collect the compound for analysis, a bent tube filled with chloride of calcium may be interposed between B and C, to absorb all traces of moisture. In this reaction 1 equivalent of nitric acid decomposes 3 equivalents of hydrochloric acid, producing 1 equivalent of the red compound ( $\text{NO}_2\text{Cl}_2$ ) (which may be termed chloro-nitric gas), 3 equivalents of water, and 1 of free chlorine.

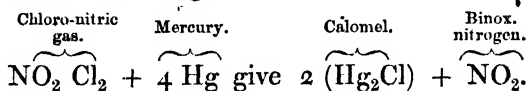


Chloro-nitric gas may be regarded as peroxide of nitrogen in which 2 equivalents of chlorine have taken the place of 2 equi-

valents of oxygen. It is a transparent, red, fuming liquid, which boils at  $19^{\circ}$  F., emitting deep lemon-yellow fumes, which have the suffocating odour of aqua regia. Water decomposes the compound immediately, appearing to dissolve it; but the solution contains hydrochloric acid and peroxide of nitrogen.



A similar decomposition ensues when it is mixed with an alkaline base, as it does not form salts: the gas ~~does not~~ be confined over mercury, since it attacks the metal instantly, forming calomel and liberating binoxide of nitrogen.



*Chloro-Nitrous Gas*, ( $\text{NO}_2\text{Cl}$ ).—When chlorine is mixed with binoxide of nitrogen in the gaseous state, they combine and form a dense orange-coloured gas; 4 volumes of the binoxide and 2 volumes of chlorine produce 4 volumes of the new compound. It cannot be formed over mercury, as it is immediately decomposed by this metal.

Aqua regia, under certain circumstances, may produce both chloro-nitric and chloro-nitrous gas, just as the deutoxide of nitrogen may, according to the circumstances under which it is mixed with oxygen, form nitrous acid, or peroxide of nitrogen. In the early stages of the decomposition of aqua regia, the product is nearly pure chloro-nitric gas ( $\text{NO}_2\text{Cl}_2$ ), but as the decomposition advances, the quantity of chloro-nitrous gas ( $\text{NO}_2 \text{ Cl}$ ) increases. Neither of these chlorine compounds exerts any solvent action upon gold or platinum.

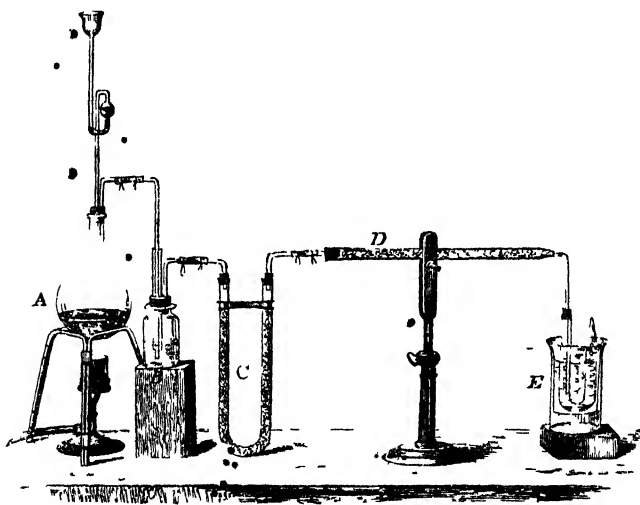
Aqua regia is largely employed as an oxidizing agent; by its action perchlorides of the metals are formed in solution, and when the liquid is decomposed by an alkali, the corresponding oxide of the metal is precipitated. By boiling the solutions of the metals in aqua regia with an excess of hydrochloric acid, the whole of the nitric acid may be decomposed and expelled, and a pure solution of the metallic chlorides with excess of hydrochloric acid will be formed.

**OXIDES OF CHLORINE.**—The affinity of chlorine for oxygen is so feeble that the two elements do not enter directly into combination. Several compounds of oxygen and chlorine may be obtained by indirect methods. Five of these oxides may here be described:—

Hypochlorous acid . . . . .	ClO
Chlorous acid . . . . .	ClO <sub>3</sub>
Peroxide of chlorine . . . . .	ClO <sub>4</sub>
Chloric acid . . . . .	ClO <sub>5</sub>
Perchloric acid . . . . .	ClO <sub>7</sub>

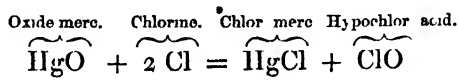
(318) HYPOCHLOROUS ACID, (ClO); *Equivalent*, 43.5; *Specific Gravity*, 2.977; *Combining Volume*, 2.—If chlorine in a perfectly dry state be passed slowly through a tube, *v.* fig. 256, filled with

FIG. 256.



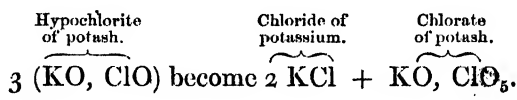
well dried oxide of mercury, obtained by precipitation from solution of corrosive sublimate by means of potash; immediate action commences; and a gas is produced which may be condensed into a liquid by surrounding the receiver, *E*, with a mixture of ice and salt. The chlorine is prepared in the flask, *A*, washed in water in the bottle, *B*, and dried by allowing it to traverse the bent tube, *C*, which is filled with pumice-stone moistened with oil of vitriol.

The reaction between the chlorine and oxide of mercury is of a very simple nature. An equivalent of chlorine displaces the oxygen from the mercury, and this oxygen at the moment of its liberation unites with a second equivalent of chlorine to form hypochlorous acid.



Hypochlorous acid is thus procured as a deep red liquid, which boils at about  $68^{\circ}$  F., emitting a vapour of a deeper colour than that of chlorine, with a peculiar suffocating chlorous smell. This gas is remarkable for the ease with which it is decomposed, the warmth of the hand causing its separation into chlorine and oxygen with explosion; 2 volumes of the acid in this way produce a mixture composed of 2 volumes of chlorine and 1 of oxygen. Its specific gravity has been found to be 2.977, which is almost exactly that which would be given by the condensation of the two gases in the proportions just mentioned, the ~~three~~ volumes occupying the space of two when combined.

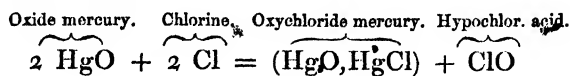
Water dissolves about 200 times its bulk of hypochlorous acid gas, and forms with it a pale yellow solution, which has an acrid, but not sour taste. In a concentrated form it is very unstable; it is rapidly decomposed when exposed to the light, bubbles of chlorine escape from it, whilst chloric acid is formed. Hypochlorous acid acts upon the metals as a powerful oxidizing agent; it attacks the skin and turns it brown; but its most important property is its bleaching power, which, according to the experiments of Gay Lussac, is twice as great as that of the chlorine in its composition. Hypochlorous acid combines with the alkalis and earths, and forms with them compounds which are decomposed even by feeble acids, such as the carbonic; the liberated hypochlorous acid shows its usual bleaching action on vegetable colours. The solutions of these salts are decomposed by gently heating them, and they become converted into a mixture of chloride and chlorate: thus—



This change is retarded by the addition of an excess of caustic alkali.

When chlorine acts upon bases which have but a feeble affinity for oxygen, these bases are often completely decomposed. In consequence of this reaction, a weak solution of hypochlorous acid is easily prepared by agitating 1 part of the red oxide of mercury with 12 of water in a large bottle of chlorine gas, care being taken that the oxide of mercury is in slight excess. The chlorine is rapidly absorbed; part of the oxide of mercury is decomposed by the chlorine, and the chloride of mercury thus produced unites with a portion of unchanged oxide of mercury, forming a brown insoluble oxychloride of that metal; and the solution on being decanted

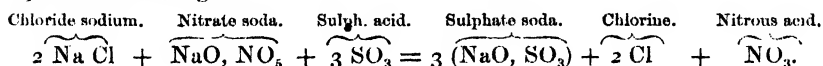
is found to contain hypochlorous acid. The reaction may be represented as follows:—



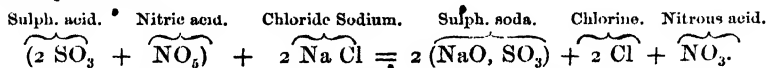
(319) *Bleaching Compounds*.—If the base upon which chlorine is made to act be a powerful one, like the alkalis or alkaline earths, the gas is absorbed, and peculiar compounds possessed of bleaching properties are produced. It is in this way that the bleaching compounds so extensively used in the arts under the names of chloride of lime, chloride of potash, and chloride of soda, are prepared.

Of these bleaching compounds the chloride of lime is the most important. It is prepared by slaking well burnt lime, and exposing it to the action of chlorine gas in layers of two or three inches in thickness, upon perforated shelves in chambers made of lead or Yorkshire flagstones. The chlorine must be gradually admitted, in order to prevent too rapid a rise of temperature consequent upon a quick absorption of the gas. Slacked lime ( $\text{CaO}, \text{HO}$ ) may in this operation be made to take up nearly half its weight of chlorine; but it is not possible to combine hydrate of lime in the form of powder with an entire equivalent of chlorine so as to form the compound  $\text{CaO Cl}$ . The product always contains a considerable excess of uncombined lime.\* Many chemists consider both this compound, and the corresponding compounds with potash and

\* A few years ago, Mr. Dunlop, of the St. Rollox Works, Glasgow, introduced a method of preparing chlorine for the manufacture of bleaching powder, by decomposing a mixture of common salt and nitrate of soda with sulphuric acid. In this operation chlorine and nitrous acid were evolved, whilst sulphate of soda was produced; the reaction may be traced by the equations following:—



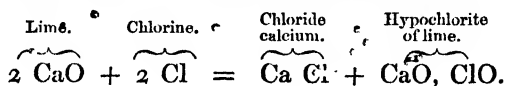
The mixed gases were made to pass through a vessel containing strong oil of vitriol, by which the nitrous acid was rapidly absorbed, whilst the chlorine passed on to the lime. A current of air was made to act on the nitrous sulphuric acid, the nitrous acid became converted into nitric acid by absorption of oxygen; and the mixed acids being made to act upon fresh chloride of sodium, without the addition of nitre, gave rise to a similar succession of decompositions:—



The nitrous sulphuric acid may also be at once made use of in the leaden chambers in the manufacture of oil of vitriol (344).

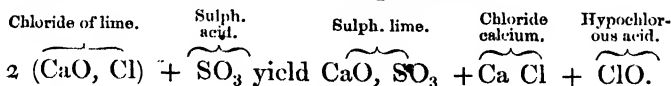


soda to be hypochlorites of the bases which enter into their formation. This however is more than questionable: they are probably direct combinations of chlorine with the oxides, or are double salts of the hypochlorite of the oxide and chloride of the metal. If the compound be supposed to be a pure chloride of lime or oxychloride of calcium, the reaction is simply an absorption of chlorine, by which the compound  $\text{CaO Cl}$ , is formed; but if it be supposed that a hypochlorite is produced, the following decomposition must occur:—



Chloride of calcium is deliquescent, and is soluble in alcohol; but bleaching powder, when properly made, is not deliquescent, and yields scarcely any chloride of calcium to alcohol.

Chloride of lime emits the peculiar odour of hypochlorous acid when exposed to the air; under these circumstances it gradually absorbs carbonic acid and exhales chlorine,—a circumstance which causes it frequently to be used as a disinfecting agent. Cloths dipped in an aqueous solution of the chloride, when hung up in the room to be fumigated, continue for many hours gradually to emit chlorine, but in quantities too small to be injurious to the inmates. Chloride of lime is only partially soluble in water, and leaves a large residue of hydrate of lime. An excess of any acid when poured upon the powder causes a free evolution of chlorine; but if the aqueous solution be mixed with half the quantity of sulphuric acid required to neutralize the lime, hypochlorous acid may be distilled off and condensed in a diluted form in a suitable receiver. The reaction which occurs may be thus represented:—



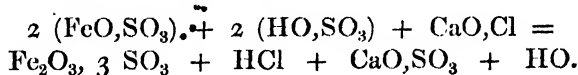
Chloride of lime is consumed in vast quantities in the bleaching of calicoes and other woven goods. The calico is well washed, and boiled successively with lime water and a weak solution of caustic soda, in order to remove the weaver's dressing, and greasy and resinous matters; it is then digested in a solution of chloride of lime, containing 2 or  $2\frac{1}{2}$  per cent. of bleaching powder. The bleaching effect of this solution is not however rendered apparent till the goods are immersed into very dilute sulphuric acid, which decomposes the chloride of lime immediately, and by liberating chlorine within the fibres of the cloth itself, rapidly removes the colour. Still, however, it is not perfectly white. The calico is therefore washed, and a second time subjected to the action of

alkali, to remove the colouring matter now rendered soluble in it by the action of the chlorine; again it is passed through a weaker solution of chloride of lime, and then through dilute acid, finally it is thoroughly washed in a copious stream of water, to remove the last traces of sulphuric acid, which would otherwise destroy the fibre.

(320) *Estimation of the Bleaching Power of Chloride of Lime.*—

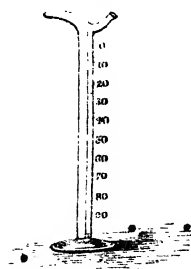
The commercial value of bleaching powder depends upon the quantity of chlorine which can be liberated from it by the addition of an acid; for it is this portion of its chlorine only which is available for bleaching purposes. Gay Lussac proposed to estimate the bleaching power by measurement of the bulk of a solution of indigo of known strength which a given weight of the chloride is able to bleach; and subsequently he proposed to determine the quantity of arsenious acid which could be converted by the bleaching powder into arsenic acid.

A still more convenient plan has been described by Mr. Graham (*Elem. Chem.* 2nd Ed. p. 592). It depends upon the determination of the quantity of a protosalt of iron which a given weight of bleaching powder in the presence of an excess of acid can convert into a salt of the sesquioxide of iron: if protosulphate of iron be used, 1 equivalent of chlorine is required for the conversion of 2 equivalents of that salt into 1 equivalent of sesquisulphate of iron; the chlorine decomposing water and becoming hydrochloric acid, while it liberates a corresponding quantity of oxygen, which combines with the protoxide of iron: thus—



Seventy-eight grains of crystallized protosulphate of iron contain a quantity of protoxide which require 10 grains of chlorine for its conversion into sesquioxide of iron. In making an experiment upon the value of a bleaching powder, 78 grains of the protosulphate are dissolved in about 2 ounces of water, and acidulated with sulphuric or hydrochloric acid; 50 grains of the bleaching powder are rubbed up in a mortar with 2 ounces of warm water, and transferred to a burette, or tall narrow tube (fig. 257), capable of holding 1000 grains of water, and graduated into 100 equal parts from above downwards. The mortar is washed with a little more water, and the washings added to the liquid in the burette, which is filled up exactly to 0°. The openings at top are closed with

Fig. 257.

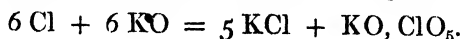


the finger and thumb, and the contents of the vessel are mixed thoroughly by agitation. The solution of chloride of lime is then added gradually to the sulphate of iron, (constantly stirring the mixture,) until the whole of the iron is peroxidized. The progress of the experiment is ascertained by means of a solution of the red prussiate of potash, which strikes a deep blue with the liquid if it contain any unchanged protosulphate. Several drops of this liquid are spotted over a white plate, and after each addition of the chloride of lime to the protosulphate, a drop of the iron solution is mixed with one of these, and the addition of the chloride is continued so long as the blue colour appears. The stronger the bleaching powder, the fewer will be the number of divisions required to be poured from the burette. This number of divisions divided by 2 will indicate the number of grains of bleaching powder which contain 10 grains of available chlorine. The strength of the powder is therefore obtained by the following proportion, in which  $m$  represents the number of measures poured from the burette:—

$$\frac{m}{2} : 10 :: 100 : x \text{ (the number of grains of chlorine in 100 grains of the powder); or } \frac{2000}{m} = x.$$

The process of converting a protoxide of a metal into one of its higher oxides, by means of chloride of lime, admits of being employed in a variety of other cases, solution of chloride of lime when mixed with hydrochloric acid, being in fact a powerful oxidizing agent. Peroxides of bismuth, of cobalt, of nickel, and of lead, may be obtained readily by adding such a mixture to solutions of the salts of these metals and heating the liquid.

(321) CHLORIC ACID, ( $\text{ClO}_5$ ); *Equivalent*, 75.5.—This compound is not known in an isolated form, as it has never been obtained with less than 1 equivalent of water as a hydrate ( $\text{HO}, \text{ClO}_5$ ). If a current of chlorine gas be caused to pass through a solution of caustic potash, it is rapidly absorbed, even when transmitted in a continuous stream, and a bleaching liquid is formed, which, on the application of heat, loses its bleaching properties, and is gradually converted into a mixture of chloride of potassium and chlorate of potash; 6 equivalents of chlorine and 6 of potash furnishing 5 equivalents of chloride of potassium, and 1 of the chlorate.



The chlorate of potash being sparingly soluble, is freed from the chloride by two or three crystallizations. In order to obtain chloric acid, the salt is decomposed by the addition of hydro-fluo-

silicic acid, which forms an insoluble compound with the potash, and chloric acid is liberated; the acid solution may be poured off from the precipitate, and concentrated by evaporation over the water bath at a heat not exceeding  $100^{\circ}$  F., till it forms a syrupy liquid of a faint chlorous smell, and a powerful acid taste. It is instantly decomposed by contact with organic matter, and in its concentrated form it chars and even sets fire to paper. By a heat of a little above  $100^{\circ}$  the acid is decomposed into oxygen gas, chlorine, and perchloric acid,  $2 \text{ Cl O}_3 = \text{Cl O}_7 + \text{O}_3 + \text{Cl}$ . In diffused daylight, it gradually undergoes spontaneous decomposition. On one occasion a small specimen sealed up in a glass tube was placed aside upon a shelf; but in a few weeks, although left untouched, the tube exploded in consequence of the expansive force of the liberated gases.

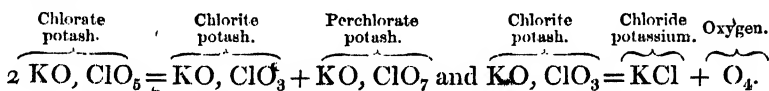
Chloric acid, when in combination, requires a higher temperature for its decomposition. The action of heat upon chlorate of potash has already been mentioned as affording a very convenient source of pure oxygen. This salt when heated to a point a little short of redness, fuses and is converted into chloride of potassium and oxygen gas,  $\text{KO, ClO}_3 = \text{KCl} + \text{O}_6$ .

This decomposition also furnishes data for ascertaining the constitution of chloric acid; for if a given weight of the chlorate be calcined, the loss indicates the entire quantity of oxygen which it contained, due both to the chloric acid, and to the potash. The proportions of chlorine and of potassium in chloride of potassium being known, the composition of chloric acid is readily calculated.

*Chlorates.*—The chlorates are monobasic salts. They are all of them decomposed by heat; oxygen is expelled, and generally a chloride of the metal is left behind; the chloride can be detected in the residue by nitrate of silver. The chlorates produce scintillation when thrown upon ignited charcoal; and when heated with combustible substances, such as phosphorus or sulphur, they explode violently; it generally happens that mere friction with these bodies is sufficient to cause a powerful detonation; for example, if half a grain of sulphur be triturated in a mortar with 2 or 3 grains of chlorate of potash, the friction is attended with a series of small explosions. When a fragment of a chlorate is placed in a drop of oil of vitriol, a yellow colour is produced, and the peculiar smell of peroxide of chlorine is evolved. All the chlorates dissolve in water, and many of them are deliquescent, and dissolve in alcohol; these solutions are not precipitated by nitrate of silver. Paper soaked in a solution of a chlorate acquires the property of smouldering on the application of a light, and burns in the same manner as touch-paper.

Chlorate of potash, when in solution, often affords a convenient method of converting the metallic protoxides into peroxides; as by the addition of hydrochloric acid to the solution, chloric acid is set at liberty, and exerts its oxidizing power. Iron, for example, which exists in a solution as a proto-salt, is thus readily converted into a persalt when the liquid is boiled.

(322) PERCHLORIC ACID, ( $\text{ClO}_7$ ); *Equivalent*, 91.5.—If instead of heating the chlorate of potash to complete decomposition, the temperature be moderated and the process stopped when one-third of the total quantity of oxygen has been expelled, the mass will have assumed a pasty condition, and will be found to contain a compound of chlorine with a still higher proportion of oxygen, to which the name of perchloric acid has been given; this compound remains in combination with the potash. The reaction appears to consist in the resolution of 2 equivalents of the chlorate into 1 equivalent of perchlorate ( $\text{KO}, \text{ClO}_7$ ) and 1 of chlorite of potash ( $\text{KQ}, \text{ClO}_3$ ), this latter salt being unable to exist at so high a temperature, is immediately converted into oxygen gas, and chloride of potassium, as follows:—

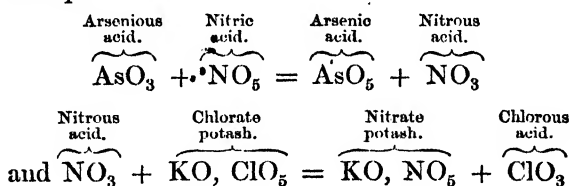


By crystallization the perchlorate of potash is readily separated from the more soluble chloride. The perchlorate dissolves in boiling water, but being very sparingly soluble at ordinary temperatures, separates in octohedra. At a red heat the perchlorate is itself resolved into oxygen and chloride of potassium. One method of obtaining perchloric acid in the form of hydrate consists in distilling the perchlorate of potash with twice its weight of sulphuric acid diluted previously with one-tenth its weight of water. If the receiver be kept cool by ice, the first portions that distil over crystallize. A large proportion of the acid, however, is decomposed into chlorine and oxygen gases. The crystals of the acid are very deliquescent; a saturated solution may be obtained of specific gravity 1.65. This solution is of a pure sour taste, and does not destroy vegetable colours; perchloric acid, indeed, is the most stable of all the oxides of chlorine. It will even dissolve iron and zinc with evolution of hydrogen gas.

Perchloric acid forms salts which all contain 1 equivalent of base. The salts of this acid in general are deliquescent. No insoluble perchlorate is known: the perchlorate of potash is the least soluble of these compounds. They are all decomposed by heat, with evolution of oxygen and formation of a chloride, but may be distin-

guished from the chlorates by not yielding a yellow gas when moistened with oil of vitriol.

(323) CHLOROUS ACID, ( $\text{ClO}_3$ ); *Equivalent*, 59.5; *Specific Gravity*, 2.646; *Combining Volume*, 2.—This substance may be obtained in the form of a gas of a deep yellowish-green colour; it is not liquefied by exposure to a cold of  $-4^\circ \text{F}$ . Chlorous acid is a dangerous compound to prepare, as exposure to a temperature not much exceeding  $130^\circ \text{F}$ . is sufficient to decompose it with a powerful explosion. Three volumes of oxygen and 2 of chlorine, if condensed into the space of 3 volumes, would yield a gas of specific gravity 2.75; Millon found it to be 2.646. This gas is soluble in about one-sixth of its bulk of water, and the solution, even when diluted very largely, has a bright yellow colour. The compound is prepared by deoxidizing chloric acid; this object is effected by means of arsenious acid when the gas is required in a state of purity. Three parts of arsenious acid and 4 parts of chlorate of potash are rubbed up into a paste with water, and 16 parts of nitric acid, of specific gravity 1.24 are added; the whole is placed in a flask, which is filled up to the neck with the mixture, and a very gentle heat is applied by means of a water bath. (Millon, *Ann. de Chimie*, III. vii. 322). The arsenious acid becomes oxidized at the expense of the nitric acid; nitrous acid is formed, and this in turn is reconverted into nitric acid by decomposing the liberated chloric acid: for example—

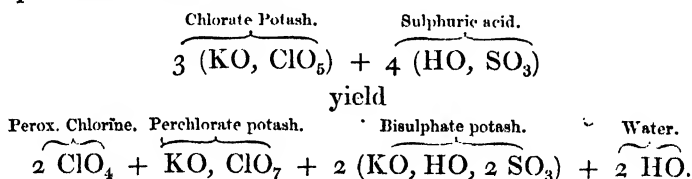


The gas must be collected by displacement in dry bottles, as it is rapidly decomposed by mercury.

Chlorous acid possesses considerable bleaching power; it forms definite salts, containing 1 equivalent of acid to 1 of base, like chlorite of potash ( $\text{KO, ClO}_3$ ). The chlorites are decomposed by the feeblest acids, such even as carbonic acid. Nitrate of lead produces a yellowish-white precipitate in their solutions, owing to the formation of a chlorite of lead ( $\text{PbO, ClO}_3$ ).

(324) PEROXIDE OF CHLORINE, ( $\text{ClO}_4$ ); *Equivalent*, 67.5; *Calculated Density*, 2.346.—This compound is also gaseous at ordinary temperatures, but by slight pressure or by exposure to a cold of  $-4^\circ \text{F}$ ., it is reducible to a red liquid, which boils, when the pressure is removed, at  $68^\circ \text{F}$ . It is of a colour still deeper than

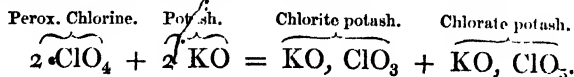
that of chlorous acid, and has a similar but less irritating odour. Water dissolves about twenty times its bulk of the gas, and forms a yellow solution, which bleaches powerfully. The gas requires great care in its preparation, as a temperature of  $140^{\circ}$  or  $145^{\circ}$  F. determines its explosion, 4 volumes of this gas furnishing a mixture of 4 volumes of oxygen and 2 volumes of chlorine. Peroxide of chlorine may be thus obtained:—fused chlorate of potash is broken into coarse fragments, and treated with two-thirds of its weight of oil of vitriol, the action being favoured by a very gentle heat. The reaction is rather complicated; 4 equivalents of sulphuric acid decompose 3 equivalents of the chlorate, 2 equivalents of the peroxide of chlorine escape, whilst 2 equivalents of bisulphate of potash and 1 of perchlorate are formed.



Peroxide of chlorine acts rapidly upon mercury, and must therefore be collected by displacement. Mere contact with many combustible matters at once determines its explosion. Place, for instance, 4 or 5 grains of chlorate of potash at the bottom of a tall glass, and pour upon it a little water; then having placed the glass in a deep plate (fig. 258), add a piece of phosphorus about the size of a pea, and by means of a long funnel pour slowly in about a tea-spoonful of oil of vitriol; flashes of a beautiful green light, attended with a crackling noise, will be immediately produced. If loaf sugar and chlorate of potash be separately powdered, and mixed in equal proportions with each other by means of a spatula, the addition of a drop of sulphuric acid



will liberate peroxide of chlorine, which will be decomposed by the combustible matter, and sufficient heat will be emitted to cause the mass to burst into flame, and to deflagrate with great brilliancy. Peroxide of chlorine is not possessed of acid properties; alkaline solutions, however, absorb it rapidly, but when evaporated, they yield a mixture of chlorite and chlorate of the base.



Other oxides of chlorine have been obtained; they have a composition which may be explained by considering them as compounds of chlorous acid with chloric or with perchloric acid; they however present but few points of interest. Davy's euchlorine, which is evolved on gently heating a chlorate with hydrochloric acid, is a yellow explosive gas, consisting of a mixture of chlorine with one of these compound oxides, the *chloro-chloric acid*, ( $2 \text{ClO}_5, \text{ClO}_3$ ).

(325) CHLORIDE OF NITROGEN.—The affinity existing between chlorine and nitrogen is very feeble, only one compound of them being known; and this is always obtained by indirect means.

When a stream of chlorine gas is transmitted through a solution of ammonia, hydrochloric acid is formed, and pure nitrogen is liberated. If the solution be concentrated, each bubble of chlorine produces a flash of light. This process is sometimes resorted to for procuring nitrogen, which only requires washing with water to remove the traces of ammonia that accompany it. One equivalent of ammonia, when decomposed by 3 of chlorine, yields 1 equivalent of nitrogen;  $\text{H}_3\text{N} + 3\text{Cl} = 3\text{HCl} + \text{N}$ .

But if instead of acting on a solution of free ammonia, a bottle of chlorine perfectly clear from greasy matter be inverted over a leaden dish containing a solution of 1 part of sal ammoniac ( $\text{H}_4\text{N Cl}$ ), in 12 parts of water, drops of a yellow oily-looking liquid gradually form on the surface of the liquid and fall to the bottom, whilst the chlorine slowly disappears: this liquid is the substance known as chloride of nitrogen; it has a specific gravity of 1.653, is very volatile, and possesses a peculiar penetrating odour. Chloride of nitrogen is one of the most dangerous compounds known, as it explodes with tremendous violence when heated to between  $200^\circ$  and  $212^\circ \text{F}$ ., emitting a flash of light when the detonation occurs. The explosion is so sudden that it invariably breaks any glass or porcelain vessel in which it may be contained: hence a leaden saucer is used in preparing the compound. Chloride of nitrogen also explodes violently at ordinary temperatures when brought into contact with many inflammable substances, such as oil of turpentine, phosphorus, and the fixed oils. The alkalis also cause its immediate explosion. On the other hand, it does not explode when touched with the resins, the strong acids, with metallic bodies in general, or with sugar.

Little or nothing is known of the cause of these remarkable reactions, or of the light and heat emitted when the chloride explodes, by slightly elevating its temperature; in this case and in the analogous instances of the explosion of the oxides of chlorine, light is emitted, not during the act of combination as is usual, but



during the expansion and sudden separation of the two gaseous elements.

The analysis of this body is attended with great difficulty; indeed considerable doubt exists as to its true composition. It is highly probable that it is not simply a chloride of nitrogen, but a combination of chlorine, nitrogen, and hydrogen ( $\text{HCl}_2\text{N} + \text{Cl}_3\text{N}$ ), somewhat analogous to the corresponding explosive compound which iodine forms. (Gladstone, *Quart. Journ. Chem. Soc.*, vol. vii., p. 59.)

(326) CHLORIDES OF CARBON.—Chlorine does not unite directly with carbon; but Dr. Faraday succeeded in procuring several compounds between these elements by the decomposition of Dutch liquid, a compound of carbon and hydrogen with chlorine, obtained under circumstances which will be explained when treating of olefiant gas (400).

*Subchloride of Carbon* ( $\text{C}_4\text{Cl}_2$ ) forms fine silky crystals, which sublime in closed vessels without change; it is soluble in ether. This substance is obtained by decomposing the protochloride of carbon ( $\text{C}_4\text{Cl}_4$ ) by causing it to pass several times through a tube heated to bright redness. It burns with a red smoky flame.

*Protochloride of Carbon* ( $\text{C}_4\text{Cl}_4$ ) was procured by Faraday from the sesquichloride ( $\text{C}_4\text{Cl}_6$ ) by subliming it repeatedly through a tube filled with fragments of glass, heated to redness. It is a colourless liquid, of sp. gr. 1.552, which boils at  $248^\circ\text{F}$ ., and gives off a vapour of sp. gr. 5.820. It therefore contains 8 volumes of chlorine vapour and 8 volumes of carbon vapour, condensed into the usual combining measure of 4 volumes: for

$$\begin{array}{rcl}
 8 \text{ vols. carbon vapour} & = 8 \times 0.4146 & = 3.3168 \\
 8 \text{ vols. chlorine vapour} & = 8 \times 2.47 & = 19.7600 \\
 & & \hline
 & & 23.0768 \\
 & & \hline
 & & 4
 \end{array}
 = 5.769$$

The *Sesquichloride of Carbon* ( $\text{C}_4\text{Cl}_6$ ) was originally obtained by the action of chlorine upon Dutch liquid (Faraday); it is a volatile crystalline solid, with an aromatic odour resembling that of camphor. It fuses at  $320^\circ$  and boils at  $360^\circ\text{F}$ .; it has a sp. gr. of 2, and is soluble in alcohol, in ether, and in the fixed and volatile oils. The density of its vapour is 8.57 (Regnault), and its combining measure is 4 volumes. An isomeric (413) liquid chloride, the vapour of which has a density of 4.082, and a composition  $\text{C}_2\text{Cl}_3$ , was obtained by Regnault by passing the vapour of bichloride of carbon ( $\text{C}_2\text{Cl}_4$ ) through a tube heated to low redness.

*Bichloride of Carbon* ( $C_2 Cl_4$ ) was obtained by Regnault from wood-spirit, from chloroform, and from other derivatives from wood-spirit, by exposing them in the sun to the action of an excess of chlorine. Kolbe also found that the vapour of bisulphide of carbon and chlorine, when passed through a porcelain tube heated to redness, yielded the same compound. It is a colourless liquid, of sp. gr. 1.599; it boils at  $172^\circ F.$ , and the density of its vapour is 5.30. It becomes a crystalline solid of pearly lustre at  $-9^\circ F.$

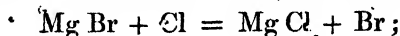
(327) OXYCHLORIDE OF CARBON: *Chlorocarbonic Acid*; *Phosgene Gas*,  $(COCl)$ ; *Equivalent*, 49.5; *Specific Gravity*, 3.68; *Combining Volume*, 2.—When equal volumes of carbonic oxide and chlorine are exposed to the direct rays of the sun they combine, and condense into half their volume. The combination takes place slowly in the diffused light of day; but no action occurs if the two gases are mixed together and kept in a dark room. Oxychloride of carbon is a colourless, suffocating gas, which is immediately decomposed by water into carbonic acid and hydrochloric acid:  $COCl + HO = CO_2 + HCl$ . It does not possess the characters of an acid; but if the gas be mixed with ammonia in the proportion of 1 volume of phosgene to 4 of ammonia, both gases are condensed, and form a white volatile solid, which is neutral to test paper, destitute of smell, soluble in water and in alcohol slightly diluted, but it is insoluble in ether. This compound is regarded by Regnault as a mixture of chloride of ammonium and of carbamide;  $2(H_3N) + COCl = H_4N, Cl + H_2N, CO$ .

## II. BROMINE.

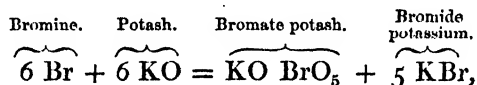
*Symbol*, Br; *Eq.*, 80; *Combining Volume of Vapour*, 2; *Specific Gravity of the Vapour*, 5.34; *of the Liquid*, at  $32^\circ F.$ , 3.187.

(328) Bromine was discovered by M. Balard in the year 1826, in *bittern*, which is the mother-liquor of sea water, after the less soluble salts have been extracted by crystallization. It exists in sea water in minute quantity, amounting generally to about one grain in each gallon. The bromine appears to be combined with magnesium, as bromide of magnesium. Many saline springs, such as those of Kreuznach and Kissingen, contain it in quantity sufficient to render its extraction from them a source of profit. Indeed few deposits of chloride of sodium exist in which traces of bromine have not been found. Berthier has also found it in a silver ore from Mexico, in which the bromide of silver is mixed with a large proportion of the chloride of silver.

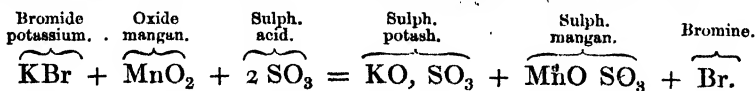
*Preparation.*—In order to obtain bromine, the mother-liquor, after all the salts separable by crystallization have been removed from the brine, is subjected to a current of chlorine, taking care to avoid an excess of this gas, which would occasion inconvenience by forming a compound with the liberated bromine. All the bromides are decomposed readily by chlorine, the affinities of chlorine being more powerful than those of bromine. In the foregoing operation chloride of magnesium is formed and bromine is set free,



the bromine shows itself by giving to the liquid a beautiful and characteristic yellow colour. This yellow liquid, if agitated with ether, parts with its bromine to the ether, which, on standing, rises to the surface, where it forms a beautiful golden yellow layer. The ethereal solution is decanted and agitated with a solution of potash. The yellow colour immediately disappears; bromide of potassium and bromate of potash form, and are dissolved in the water,



whilst the ether, after repose, rises again to the surface despoiled of its bromine, and may be again employed in a repetition of the process upon a fresh quantity of bittern. When the solution of potash has, by repeated charges of bromine, been nearly neutralized, the liquid is evaporated to dryness; the saline mass is gently ignited to decompose the bromate, after which it is mixed with peroxide of manganese and distilled in a retort with sulphuric acid: dense red vapours of bromine pass over, which may be collected in a receiver containing water, and kept cool by ice. The decomposition is of the same nature as that attending the formation of chlorine from sea-salt, by means of oxide of manganese and sulphuric acid:—



In this operation a small quantity of chlorine passes over with the bromine, as, from the manner in which the bromide of potassium is formed, it is always contaminated with a portion of the chloride. The chlorine unites with part of the bromine, forming chloride of bromine, which is partially decomposed and dissolved by the water in the receiver, while the bromine condenses in red drops. In order to obtain bromine free from chlorine it must

be saturated with hydrate of baryta, which produces a mixture of bromide and chloride of barium with bromate of baryta; this mixture is heated to redness to convert the bromate into bromide; and the residue is digested in alcohol, which dissolves nothing but the bromide. The bromide of barium is obtained by evaporation, and when heated with manganese and sulphuric acid it yields pure bromine.

*Properties.*—Bromine forms a red liquid, so deep in colour as to be nearly opaque. It has a sp. gr. of 2.966 at 60°; it is extremely volatile, and emits dense red vapours resembling peroxide of nitrogen in colour. In smell it resembles chlorine, and is extremely irritating to the nose and fauces when respired, even if largely diluted with air. When swallowed it operates as a powerfully irritating poison; it acts rapidly on all the organic tissues, and renders the skin permanently yellow. Bromine boils at 145°.4 F. (Pierre), and when exposed to a cold of 9°.5 F. it forms a red crystalline solid. The properties of bromine greatly resemble those of chlorine, though they are less strongly developed. It bleaches many vegetable colours. Its vapour will not support the flame of a burning taper. Bromine is slightly soluble in water, and gives to it a yellow colour; it also forms with it a hydrate ( $\text{Br} + 10 \text{HO}$ ) (Löwig,) which crystallizes in octohedra at 32° F. Alcohol dissolves bromine freely, and ether does so still more abundantly. Bromine combines directly with many of the metals, and forms bromides, the act of combination being often attended with ignition; even gold slowly combines with it. Bromine often combines with the same metal in more than one proportion, and the compounds of bromine correspond almost always, both in number and composition, with those of chlorine with the same metal. Oxybromides may be formed resembling the oxychlorides; and the bromides of the alkaline metals form double bromides with the bromides of the metals which yield acids with oxygen.

(329) HYDROBROMIC ACID, ( $\text{HBr}$ ); *Equivalent*, 81; *Specific Gravity*, 2.71; *Combining Volume*, 4.—Bromine resembles chlorine in its power of combining with hydrogen, and forming with it a very powerful acid, which is a gaseous body consisting of equal measures of hydrogen and bromine vapour united without change of bulk. The mixture of bromine vapour and hydrogen cannot be detonated by the approach of flame, or by the electric spark, but the two elements may be made to unite slowly, by suspending a red-hot platinum wire in the mixture. If moisture be present the occurrence of combination instantly shows itself by the formation of

white fumes, which result from the union of the newly-produced gaseous acid with the aqueous vapour.

Hydrobromic acid gas may be procured abundantly by decomposing bromide of potassium with a concentrated solution of phosphoric acid. If sulphuric acid be used for the purpose, the product is impure, as this acid itself undergoes partial deoxidation. The gas is colourless, it is not inflammable, it extinguishes flame, and possesses the usual irritating action of acid gases on the lungs. It is very soluble in water, forming, when concentrated, a fuming solution of greater density than hydrochloric acid. A solution of the acid of sp. gr. 1.486 (HBr, 10 HO) contains about 47 per cent. of the anhydrous acid, it boils at 259° F., and may be distilled without change. Chlorine decomposes it immediately; bromine being set free and hydrochloric acid produced.

The action of hydrobromic acid upon the metallic oxides is analogous to that of hydrochloric acid upon them; bromide of the metal and water being produced; thus hydrobromic acid and potash combine, and form bromide of potassium and water:  $KO + HBr = KBr + HO$ .

*Bromides.*—The bromides are all solid at ordinary temperatures; most of them fuse easily at a moderate heat, and are partially volatilized; and the bromides of gold and platinum are decomposed. Most of the bromides dissolve readily in water, and when in solution they may be recognised by the yellow colour of bromine which is produced by the addition of a few drops of chlorine water. On agitating the yellow solution with ether the bromine dissolves in the ether, which on standing separates as a yellow liquid at the top of the colourless aqueous portion. The bromides, when heated with black oxide of manganese and oil of vitriol, yield red vapours of bromine. Nitrate of silver and nitrate of lead each give a white precipitate with the bromides, forming bromide of silver (AgBr), or bromide of lead (PbBr); the bromide of silver is insoluble in nitric acid, but is dissolved by an excess of ammonia; but the bromide of lead dissolves when dilute nitric acid is added. Sub-nitrate of mercury also gives a white precipitate of dibromide of mercury (Hg<sub>2</sub>Br) when added to solutions of the bromides.

(330) BROMIC ACID, (BrO<sub>5</sub>); *Equivalent*, 120.—Only one compound of bromine with oxygen is known; and this has never been obtained free from water; it forms an acid corresponding to chloric acid in composition. Bromate of potash is procured by acting on bromine with caustic potash, and from this salt the acid is obtained by a process similar to that for chloric acid. By the

action of heat, bromate of potash is decomposed, bromide of potassium being formed, whilst oxygen is liberated. Bromates of silver, of lead, and of mercury, are sparingly soluble. All the salts of this acid which have as yet been prepared are monobasic.

*Chloride of Bromine* is easily prepared by transmitting chlorine gas through liquid bromine: it is a volatile, reddish-yellow liquid, with a pungent, irritating odour. Water dissolves it, forming a deep yellow solution possessed of considerable bleaching power.

With nitrogen, bromine forms a detonating oily looking liquid, resembling chloride of nitrogen in appearance and properties.

### § III. IODINE.

*Symbol, I; Equivalent, 126.8; Combining Volume, 2;  
Specific Gravity of Vapour, 8.716.*

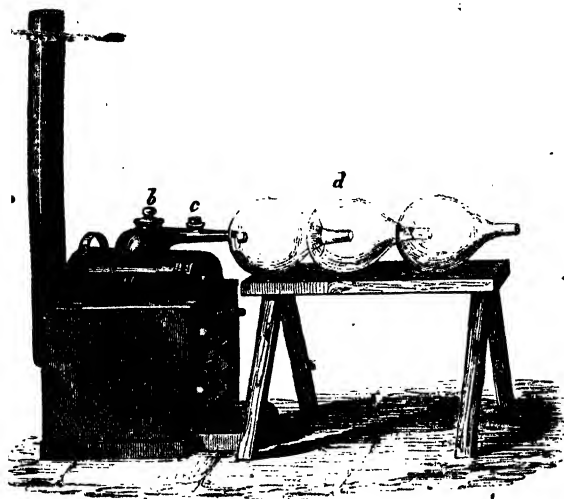
(331) Iodine, the third element in the group which we are now examining, is still denser than bromine, as it assumes the solid form at the ordinary temperature of the air. Its discovery dates back to the year 1811, when it was found by Courtois accidentally in the waste liquors produced in the manufacture of soda from the ashes of sea-weed.

Iodine exists in the ocean in quantities still smaller than bromine. It is, notwithstanding, obtained with less difficulty, as it is extracted from sea water, and stored up by marine plants, such as the fuci, algæ, and sponges. These, when burnt, give an ash which is technically known as *kelp*; it contains iodine in the form of iodide of sodium. In the mineral kingdom, iodine has been found in one or two rare ores, thus it occurs combined with silver in Mexico, and with zinc in Silesia.

*Preparation.*—Iodine is at present largely manufactured at Glasgow, from kelp made on the coasts of Scotland and Ireland: the following is an outline of the process adopted in procuring it (Graham, *Elem. Chem.* 2nd Ed. p. 492): The sea-weed having been dried in the sun, is burned in shallow excavations, at a low heat; owing to the volatility of the iodide of sodium at a red heat, the loss of this salt would be considerable if the temperature were allowed to rise too high. The half fused ash or kelp which remains is broken into fragments and treated with boiling water, which dissolves about one-half of the ash. The liquid thus obtained is then evaporated in open pans, and all that can be separated by crystallization is removed; sulphate of soda; carbonate of soda, and

chloride of potassium are thus extracted. The iodine remains in the mother-liquor, which still retains sulphide of sodium, besides sulphite, and some carbonate of soda. This liquor, or iodine ley, is now mixed with one-eighth of its bulk of oil of vitriol, and allowed to stand for twenty-four hours; carbonic acid, sulphurous acid, and sulphuretted hydrogen gases escape, and sulphate of soda again crystallizes out, mixed with a considerable quantity of deposited sulphur. The supernatant liquid is next trans-

FIG. 259.

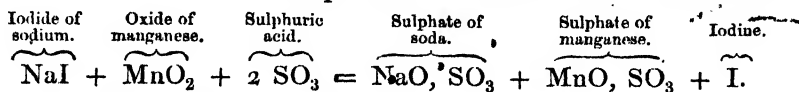


ferred to a leaden retort of cylindrical form, *a*, fig. 259, supported in a sand bath, and gently heated from beneath by a small fire; the head of the retort, *b c*, is luted on with clay, and the contents of the retort having been heated to about  $140^{\circ}$ , a quantity of powdered binoxide of manganese is introduced

through the tubulure *b*. The temperature may be gradually raised, <sup>but must be kept below  $212^{\circ}$</sup>  ~~to  $212^{\circ}$ , but not higher~~; iodine distils over and is condensed in the globular receivers, *d*. It is purified by a second sublimation. The object of the second tubulure, shown at *c*, is to facilitate the clearing of the neck of the retort in case it should become obstructed by the formation of crystals. If the temperature be allowed to rise above  $212^{\circ}$ , chlorine is disengaged and combines with part of the iodine, forming chloride of iodine.

In the foregoing process, the addition of the sulphuric acid occasions the decomposition of the carbonate, sulphite, and hyposulphite of soda which still remain in solution, as well as of any sulphide of sodium that may be present, forming sulphate of soda which is removed by crystallization. The liquid retains an excess of sulphuric acid, and all the iodide of sodium. When this mixture is heated with peroxide of manganese, the iodine

is liberated, whilst sulphate of soda and sulphate of manganese remain in the retort. The process resembles that for bromine.



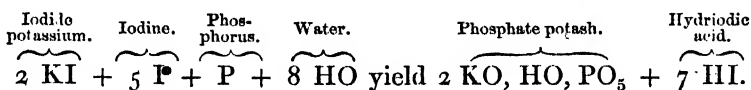
*Properties.*—The crystalline form of iodine is an octohedron with a rhombic base; but it is generally obtained in bluish black scales, resembling plumbago in lustre. It is a non-conductor of electricity. At ordinary temperatures, and especially when in a moist condition, it is sensibly volatile, emitting an odour like that of chlorine, but much weaker. In the solid form it has a specific gravity of 4.947; when heated it undergoes fusion at  $225^{\circ}$ ; at about  $347^{\circ}$  it boils and is converted into a magnificent purple vapour, from which it derives its name (*ιώδες*, 'violet-coloured'). Iodine, when taken internally, acts in large doses as an irritant poison; but in small quantities it is a most valuable medicine, particularly in glandular swellings, and in certain forms of goitre. It stains the skin and most organized substances, of a brown colour, and gradually corrodes them. Water forms with it a yellow solution, but dissolves it only in very small quantity. Its bleaching properties are very feeble. Alcohol, ether, and solutions of the iodides dissolve it freely. *Lugol's Solution*, which was formerly much used in medicine, consists of 20 grains of iodine and 30 of iodide of potassium, dissolved in an ounce of water; it is of a deep brown colour. Iodine attacks the metals rapidly; iron or zinc is readily dissolved by it if placed with it in water, an iodide of the metal being formed. All the compounds of iodine with the metals and with hydrogen are decomposed by chlorine, and even by bromine, while the iodine is set free. Advantage is taken of this fact in ascertaining the presence of iodine. The most delicate test for it, when uncombined, is the intense blue colour which it strikes with starch; by its means, with due precaution, 1 part of iodine, when dissolved in one million parts of water, may be discovered.

There are various modes of applying this test: the simplest consists in mixing a little cold starch paste with the liquid which is suspected to contain iodine; if it be present in an uncombined form, a beautiful blue colour shows itself. If the iodine be in combination, this colour does not appear until a drop of chlorine water or of solution of bleaching powder be added to set the iodine free. An excess of chlorine must be avoided, as it forms chloride of iodine, and prevents the action of the test. The colour also fades away if the solution be heated, but it is partially restored as



the temperature falls. As starch paste cannot be long kept without undergoing decomposition, it is often convenient to substitute for the freshly made paste, paper which has been smeared with the starch, and allowed to become dry. If kept in a dry place such paper may be preserved for an indefinite length of time, and is ready for use at any moment.

(332) HYDRIODIC ACID, (HI); *Equivalent*, 128; *Specific Gravity*, 4.443; *Combining Volume*, 4.—By heating iodine in hydrogen, the volume of the gas becomes doubled, and a colourless acid gas is produced. It fumes in the air, is very soluble in water, and possesses a pungent irritating odour; but the gas is never prepared for use in this manner. A better mode is the following: place in a small retort 10 parts of iodide of potassium with 5 of water, add 20 of iodine; then drop in cautiously 1 part of phosphorus cut into small fragments, and apply a gentle heat. Hydriodic acid gas will be extricated abundantly, and may be collected, by displacement, in dry bottles. The result of the reaction is explained by the following equation:—



Hydriodic acid gas is not combustible, nor does it support combustion. It is reduced under strong pressure to a yellowish liquid, which freezes at  $-60^{\circ}$  F.

A solution of hydriodic acid may be easily prepared by suspending iodine in water, and transmitting a current of sulphuretted hydrogen gas through the mixture until the brown colour of the iodine disappears. Sulphur is deposited in abundance, and hydriodic acid is formed. The liquid gradually becomes clear if left at rest; it may then be decanted from the precipitated sulphur: the decomposition consists simply in the displacement of the sulphur by the iodine;  $\text{HS} + \text{I} = \text{HI} + \text{S}$ . This liquid may be concentrated till it consists of  $\text{HI} + 11 \text{ H}_2\text{O}$ ; it acquires a density of 1.7. It then distils unchanged at  $262^{\circ}$  F. It is a powerful acid, and dissolves iodine freely, forming a brown solution: by exposure to the air, especially if placed in a strong light, it absorbs oxygen, water is formed, and the liquid becomes brown from the liberation of iodine. Chlorine effects its instant decomposition, whether it be in the gaseous form or in solution. Mercury decomposes it gradually, and combines with its iodine.

The composition of hydriodic acid may be ascertained by heating potassium in a measured volume of the gas. Iodide of potas-

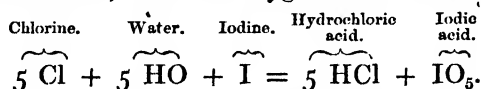
sium is formed, and hydrogen remains equal in bulk to half the acid gas employed.

*Iodides.*—The iodides of the metals are all solid at ordinary temperatures; they are less fusible and volatile than the corresponding chlorides and bromides. The iodides of gold, silver, platinum, and palladium are decomposed by heat alone, and most of the iodides are converted into oxides when heated in the air,—the oxygen displacing the iodine. The greater number of the metallic iodides dissolve freely in water, though some are insoluble, and exhibit colours of great brilliancy. The soluble iodides of the metals, or hydriodates of the metallic oxides, as they were formerly termed, may be obtained by the direct combination of hydriodic acid with the metallic oxide, or by the action of iodine and water upon the metal itself. These iodides, when in solution, are characterized by the reaction with starch already mentioned: with a solution of corrosive sublimate (chloride of mercury) ( $\text{Hg Cl}$ ), they give a beautiful salmon-coloured precipitate, which almost immediately changes to a brilliant scarlet. This is the iodide of mercury; it is soluble in excess both of iodide of potassium, and of corrosive sublimate. Subnitrate of mercury gives a green precipitate in solutions of the soluble iodides. With nitrate of lead a bright yellow precipitate of iodide of lead is formed; it is slightly soluble in boiling water, especially if the lead salt be present in excess; on cooling, the iodide of lead separates in very beautiful silky scales. With nitrate of silver, a buff-coloured iodide of silver, nearly insoluble in ammonia, is formed. If a mixture of proto-sulphate of iron and sulphate of copper be added to a solution of any iodide, a white subiodide of copper precipitates: with chloride of gold the iodides give a lemon-yellow precipitate, and with salts of palladium a brown iodide of palladium is produced, which is sometimes used for ascertaining the quantity of iodine present in a solution in which it occurs mixed with chlorine, as chloride of palladium is freely soluble in water.

(333) *Oxides of Iodine.*—Iodine has a more powerful affinity for oxygen than either chlorine or bromine, and forms with it two well-defined acids, viz., the iodic acid ( $\text{IO}_5$ ) and the periodic acid ( $\text{IO}_7$ ), besides some other oxides but imperfectly known.

*Iodic Acid, ( $\text{IO}_5$ ); Equivalent, 167.*—This acid corresponds in composition to chloric and bromic acids. It may be prepared in several ways: thus it may be procured by long boiling of iodine in concentrated nitric acid: Millon's method consists in mixing equal parts of chlorate of potash and iodine with 5 parts of water

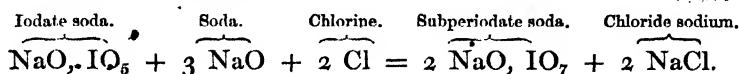
and a little nitric acid. Chlorine is evolved in abundance, and iodate of potash is formed which dissolves in the liquid: chloric acid is set free by the nitric acid, and imparts its oxygen to the iodine, chlorine gas escaping, while the iodic acid liberates a fresh portion of chloric acid from the chlorate, and this undergoes a similar decomposition. Liebig's plan of preparing iodic acid consists in suspending iodine in water, and transmitting through it a current of chlorine gas till the iodine is dissolved; the liquid is then neutralized by carbonate of soda, when a copious precipitate of iodine is formed, which may be again similarly treated by chlorine. In this case the chlorine decomposes water, taking the hydrogen to form hydrochloric acid, while the oxygen is transferred to the iodine.



The neutralized liquid contains iodate of soda and chloride of sodium. Chloride of barium is next added; an abundant precipitate of iodate of baryta, which is but sparingly soluble, is formed; this is washed from adhering salts, and is decomposed by a quantity of sulphuric acid just sufficient to combine with the baryta. Iodic acid dissolves in the water, whilst the insoluble sulphate of baryta separates. The iodic acid, by evaporation, may be obtained in crystals composed of  $\text{HO}, \text{IO}_5$ : by a heat of  $360^\circ \text{ F.}$  it is rendered anhydrous, and at about  $700^\circ \text{ F.}$  it is decomposed into iodine and oxygen. Its solution is destitute of odour, and has a sour astringent taste. Organic bodies decompose it, and owing to this circumstance litmus paper is first reddened and afterwards bleached by it.

**Iodates.**—Some iodates contain 1 equivalent, some 2, and some 3 equivalents of acid to 1 equivalent of base: for example, the three iodates of potash may be represented by the following formulæ:—the neutral iodate,  $\text{KO}, \text{IO}_5$ ; the biniodate,  $\text{KO}, 2 \text{ IO}_5$ ; and the teriodate,  $\text{KO}, 3 \text{ IO}_5$ . All the iodates are decomposed by heat, and give off oxygen. If the metal have a stronger affinity for iodine than for oxygen, an iodide of the metal is formed; thus  $(\text{KQ}, \text{IO}_5)$ , iodate of potash, becomes  $\text{KI} + 6 \text{ O}$ : but if the affinity of the metal be greater for oxygen than for iodine, the oxide is left behind: iodate of baryta, for example, is converted into baryta, oxygen gas, and free iodine,—the latter escapes in purple vapours;  $\text{BaO}, \text{IO}_5 = \text{BaO} + \text{O}_5 + \text{I}$ . The aqueous solutions of the iodates are decomposed by sulphurous acid;  $\text{KO}, \text{IO}_5 + 6 \text{ SO}_2 = \text{KI} + 6 \text{ SO}_3$ ; an iodide of the metal is formed, and then the iodine may be discovered by the starch test in the usual way. Iodic acid forms crystallizable compounds with the sulphuric and many other acids.

(334) PERIODIC ACID,  $\text{IO}_7$ , *Eq.* 183.—This acid corresponds in composition to the perchloric. It is obtained by transmitting a current of chlorine gas through a solution of iodate of soda containing caustic soda, in the proportion of 3 equivalents of free alkali to 1 of iodate of soda; a sparingly soluble basic periodate of soda is formed. The reaction which occurs consists in the decomposition of 2 equivalents of soda by 2 of chlorine, chloride of sodium being formed, whilst the 2 equivalents of oxygen combine with the iodic acid to form the periodic acid; the latter combines with a second equivalent of soda, and forms the basic periodate of soda; as explained by the following symbols:—



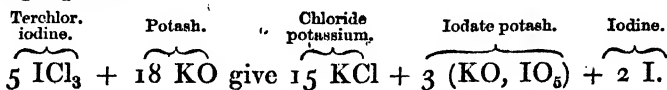
The basic periodate of soda is dissolved in dilute nitric acid, and precipitated by the addition of nitrate of silver; the periodate of silver is then dissolved in boiling nitric acid; a neutral periodate of silver crystallizes as the liquid cools, and this salt when treated with water is decomposed into basic periodate of silver, which is insoluble, and periodic acid, which dissolves. By evaporation of the solution the periodic acid may be obtained in deliquescent crystals, which contain 5 equivalents of water, and are somewhat soluble in alcohol and ether. The periodates are most of them sparingly soluble in water, but dissolve freely in dilute nitric acid. Solution of the neutral soda salt ( $\text{NaO, IO}_7$ ) causes a precipitate of basic periodate with solutions of neutral salts of baryta, of lime, of lead, or of silver, whilst the liquid becomes acid. The basic silver salt is pale yellow if precipitated from cold, but red if from hot solutions.

(335) CHLORIDES OF IODINE.—Two compounds of iodine with chlorine, a protochloride and a terchloride, may be obtained.

The *protochloride* ( $\text{ICl}$ ), *eq.* 162.5, is a very irritating volatile yellowish brown liquid, which is obtained by distilling 1 part of iodine with 4 of chlorate of potash; the distilled chloride of iodine dissolves, apparently without change, in water, in alcohol, and in ether. This chloride when hot dissolves iodine readily, and deposits it in beautiful crystals.

*Terchloride of iodine* ( $\text{ICl}_3$ ), *eq.* 233.5; this compound is formed by acting upon iodine with excess of dry chlorine gas. It forms magnificent ruby red crystals, which sublime spontaneously in closed bottles; the vapour is extremely irritating to the eyes. If exposed to the air it attracts moisture, and it dissolves in water unchanged. Alkaline solutions decompose it, and iodine is precipitated.

pitated; if heated with potash, for example, chloride of potassium and iodate of potash are produced in the manner explained by the following equation:—

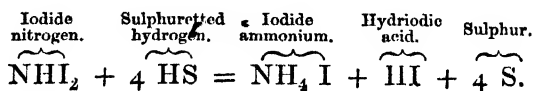


Iodine also combines with bromine, and forms compounds with it which are possessed of properties similar to those of the chlorides of iodine.

(336) IODIDE OF NITROGEN, ( $\text{NHI}_2$ ). This substance may be obtained as a black powder by digesting iodine for half an hour in a cold solution of ammonia. The brown supernatant liquid, which contains excess of iodine held in solution by hydriodate of ammonia, is decanted, and the insoluble powder is placed upon filtering paper in quantities of a grain or less, and allowed to dry spontaneously. When dry, it explodes upon the slightest touch, and it indeed often detonates without any assignable cause; the explosion is remarkably sharp and sudden, fumes of iodine are produced, and a faint light is emitted.

The experiments of Bineau, the results of which have been subsequently confirmed by Gladstone, have shown that this detonating compound is not a mere iodide of nitrogen, but that it contains hydrogen also, having the formula  $\text{NHI}_2$ . The mode of its preparation admits of easy explanation by the annexed formula:  $4 \text{ I} + 3 \text{ H}_3\text{N} = 2 (\text{H}_4\text{NI}) + \text{NHI}_2$ , the reaction of 4 equivalents of iodine upon 3 of ammonia producing 2 equivalents of hydriodate of ammonia, and 1 of the detonating substance. Bunsen assigns to it the formula ( $\text{NH}_3, \text{NI}_3$ ), but it is more probable that the composition attributed to it by Bineau (*Ann. de Chimie*, III. xv. 71) is correct.

Iodide of nitrogen slowly decomposes in water; ammonia retards, but potash and the acids accelerate the decomposition; chlorine, bromine, and strong nitric acid destroy it rapidly; sulphuretted hydrogen also quietly but completely effects its decomposition. The results of this reaction afford a means of ascertaining the relative quantities of nitrogen and iodine contained in the iodide: 1 equivalent of the black powder, when treated with 4 of sulphuretted hydrogen, furnish 1 equivalent of iodide of ammonium, 1 of hydriodic acid, and 4 of sulphur:—



It is impossible not to be struck with the close analogy presented by the three elementary bodies, chlorine, bromine, and iodine, both in their uncombined state and in their compounds: they indeed form one of the best defined natural groups. At the time when iodine was discovered, chlorine was by most chemists regarded as a compound of muriatic acid and oxygen, and was consequently known as oxymuriatic acid. Indeed, most of the reactions which it presented admitted of a simple explanation on this hypothesis, and this circumstance prevented chemists from adopting generally the views which had a short time previously been put forward by Davy, maintaining the elementary nature of chlorine. The discovery of iodine, however, decided them, and assisted materially in fixing the opinion now entertained respecting the compounds of fluorine, the fourth member of the group, and of which our knowledge is in a much less satisfactory condition.

#### § IV. FLUORINE.

*Symbol, F; Equivalent, 19; Theoretical Density, 1.31;  
Combining Volume, 2.*

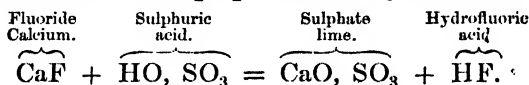
(337) Many unsuccessful attempts have been made at various times to insulate this body. Its affinities appear to be so powerful, and its action on the human frame is so irritating and deleterious, that little that is satisfactory is known concerning it in its free state. Vessels of fluorspar are the only ones which have yet been found capable of withstanding its action. No doubt, however, is entertained of its general nature, as its compounds are closely analogous to the corresponding ones of the three elements which have just been described.

Fluorspar, or fluoride of calcium ( $\text{CaF}_2$ ), is the only compound of fluorine which exists native in abundance, and from it all the preparations of fluorine are obtained. A variety of minerals contain small quantities of fluoride of calcium, particularly the phosphates of lime and certain kinds of mica. It exists too in minute quantity in the bones of animals, and especially in the teeth.

(338) **HYDROFLUORIC ACID:** *Fluoric Acid*, ( $\text{HF}$ ); *Equivalent, 20.*—Fluorine is not known to form any oxide, but with hydrogen it forms a very remarkable acid. Owing to the powerfully corrosive action which this compound exerts upon glass, which it deprives of its silicon, it is necessary always to prepare it in metallic vessels. In the construction of these vessels lead, from

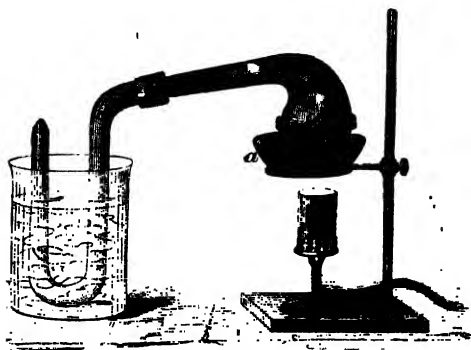
its cheapness, is preferred; but when the acid is required to be in a state of perfect purity platinum must be used, the cheaper metals being all more or less attacked by the acid.

In order to procure hydrofluoric acid in solution in a concentrated form, 1 part of finely powdered fluorspar, free from silica and the metallic sulphides, is mixed with 2 parts of oil of vitriol; at ordinary temperatures no evolution of vapour occurs if the fluorspar be pure, but a transparent gelatinous mass is formed. On the application of a gentle heat dense acid fumes of an extremely deleterious nature arise, and a reaction takes place similar to that which occurs in the preparation of hydrochloric acid: thus,



For ordinary purposes the distillation may be conducted in a leaden retort. For the convenience of removing the charge after the operation is over, it is found advantageous to make the retort in two

FIG. 260.



pieces, a head and a body; the head, *c*, fig. 260, fits accurately by an overlapping grooved joint into the body, *b*. The heat may be conveniently applied in an equable manner by placing the body of the retort in a shallow iron tray, *a*, filled with sand: *d* is the receiver for the acid; it consists of a leaden pipe fitted

by grinding to the neck of the retort, and is cooled by immersion in a mixture of ice and salt. When a perfectly pure acid is required, the still must consist of platinum. Hydrofluoric acid is a densely fuming, volatile, colourless liquid, which boils at about 60°, and remains unfrozen at -4° F. The preparation of the acid must be conducted with the greatest care, and special provision must be made for carrying off the fumes from the operator. The liquid acid is highly dangerous from its caustic action upon the skin; the smallest drop occasioning a deep and painful burn. Indeed, it ought never to be preserved in the concentrated form. When poured into water it combines with it with great avidity, and with

the evolution of so high a temperature, as to produce a hissing noise, resembling that caused by quenching a red-hot iron. In its concentrated form it has a specific gravity of 1060, but by the addition of water the density may be increased to 1150, beyond which point further dilution is attended with a regular decrease in density. The acid of sp. gr. 1150 is a quadrihydrate ( $\text{HF}, 4 \text{HO}$ ) it boils at  $248^{\circ} \text{F.}$ , and distils unchanged. Diluted hydrofluoric acid gradually dissolves the metals, extricating hydrogen. Potassium if thrown into the strong acid decomposes it with explosion.

The concentrated acid above described was long believed to be anhydrous; but the researches of Louyet (*Comptes Rendus*, xxiv., 434) have proved that it contains water. He distilled it with excess of anhydrous phosphoric acid: the water was thereby removed, and a colourless gas of an extremely irritating nature was set free; it produced dense fumes on escaping into the air, had but little action on perfectly dry glass, and was rapidly condensed by water. Fremy states that, by means of a freezing mixture of ice and salt, he obtained the anhydrous acid in the form of a colourless, mobile, very volatile liquid.

Hydrofluoric acid is easily recognised by its corrosive action upon glass. In order to detect a fluoride in a compound which is suspected to contain it, the material is reduced to a fine powder and mixed in a platinum capsule with strong sulphuric acid; a slip of glass is warmed and rubbed over with bees' wax so as to coat it uniformly; a few characters are then traced with a point through the wax, so as to expose a portion of the glass; this etching is then inverted over the platinum capsule, which is gently warmed for a few minutes, and the glass is cooled, if necessary, with a little moistened filtering paper, in order to prevent the wax from being melted. If fluorine be contained in the mixture, the characters will be found corroded on cleaning off the wax with a little oil of turpentine: if the traces be very faint, they may be rendered visible by breathing upon the surface of the plate.

A weak solution of the acid is often employed for etching on glass with advantage: in this way, for instance, the graduations on the glass stem of a thermometer may be made with great precision and facility; the glass tube is first coated with engravers' etching varnish, the divisions are traced through the varnish with a fine point, and the tube is plunged into a long leaden tube filled with the dilute acid; in the course of a few minutes the scale is permanently engraved.

. *Fluorides*.—The fluorides of the metals fuse easily on the



application of heat. A large number of them are insoluble, or only sparingly soluble in water. The solutions of the soluble fluorides corrode the glass vessels in which they are contained: they give no precipitate with nitrate of silver, since fluoride of silver is soluble; but with salts of lead, barium, magnesium, and calcium, insoluble precipitates, consisting of the fluorides of these metals, are produced. The fluoride of calcium is so transparent as to be perceived with difficulty. Many metallic fluorides combine with an additional equivalent of hydrofluoric acid and form compounds, which in many cases may be obtained in crystals that dissolve in water. The fluoride of potassium and hydrofluoric acid (KF, HF) has been used by Fremy as a convenient means of obtaining anhydrous hydrofluoric acid. By the application of heat this salt can be obtained free from water, and by a stronger heat it gives up the equivalent of hydrofluoric acid which it contains, leaving the fluoride of potassium behind. Double fluorides of the alkaline metals with the fluorides of the electro-negative metals which form acids with oxygen, may likewise be obtained with facility. Many insoluble metallic acids, such as the columbic, the titanic, molybdic, and tungstic acids are thus dissolved by hydrofluoric acid, fluorides of the metals being formed, whilst the oxygen of these compounds produces water with the hydrogen of the hydrofluoric acid: the metallic fluorides so formed dissolve in the excess of hydrofluoric acid and give rise to new compound acids. Titanic acid for instance thus forms fluotitanic acid,  $\text{TiO}_2 + 3 \text{HF} = \text{HF}, \text{TiF}_2 + 2 \text{HO}$ .

Hydrofluoric acid, when mixed with nitric acid, readily dissolves silicon which has not been strongly ignited; but it is remarkable that the mixture does not dissolve gold or platinum.

Many other compounds of fluorine have been prepared, but they are not of sufficient practical importance to require notice here: the compounds which it forms with silicon and boron will be described hereafter (389, 394).

(339) *Determination of the Equivalent of Fluorine.*—Although the chemist may be said to be entirely unacquainted with the properties of uncombined fluorine, yet its equivalent number has been determined with precision; and the mode of proceeding offers an instructive illustration of the resources of analysis in such a case.

The method of operating is as follows:—Pure fluorspar is reduced to an impalpable powder and dried; 100 grains are accurately weighed into a platinum crucible, the weight of which has been carefully determined, and sulphuric acid, also perfectly

pure, is added in sufficient quantity to reduce the whole to the consistence of cream; after standing for some hours, the excess of acid is expelled by the heat of a lamp; the temperature is raised very cautiously, and the crucible and its contents are finally heated to bright redness. In this operation the whole of the fluorine is expelled in the form of hydrofluoric acid, the calcium combining with the oxygen of the water in the oil of vitriol, whilst the fluorine unites with the hydrogen; the lime formed unites with an equivalent of sulphuric acid, and forms sulphate of lime, which remains behind. On weighing the crucible after the experiment is completed, it will be found to amount to 174·36 grains.

Now it is known that 68 grains of sulphate of lime contain 20 of calcium, 40 of sulphuric acid, and 8 of oxygen; 20 being the equivalent number of calcium:

$$\text{but } 68 : 20 :: 174\cdot36 : x (= 51\cdot25);$$

174·36 grains of sulphate of lime must consequently contain 51·25 of calcium; 100 parts, therefore, of fluorspar, if it consist only of fluorine and calcium, must be composed of 51·25 calcium and 48·75 of fluorine. The equivalent of fluorine is then found directly by the following calculation:—

Qty. of Calcium in 100 parts.	Eq. of Calcium.	Qty. of Fluorine in 100 parts.	Eq. of Fluorine.
51·25	: 20	: 48·75	: 19

The equivalent number of fluorine is thus ascertained to be 19.

## CHAPTER VII.

### SULPHUR—SELENIUM—PHOSPHORUS.

THE next group of elements comprises three substances, sulphur, selenium, and phosphorus, which are characterized by a powerful attraction for oxygen. Between sulphur and selenium a marked analogy in chemical characters is observable. Another body of comparatively rare occurrence, viz., tellurium, properly belongs to this group. The properties of selenium are intermediate between those of sulphur and tellurium, which latter presents so much of the external characters and appearance of a metal, that it is usually described with the metals.

## § I. SULPHUR.

*Symbol, S; Equivalent, 16; Combining Volume,  $\frac{1}{2}$ ; Specific Gravity of Vapour, 6.617.*

(340) Most of the sulphur used in England is obtained from Sicily, where it occurs in the native or uncombined state in beds of a blue clay formation, stretching from the southern coast of the island towards the base of Mount Etna. It is found abundantly also in volcanic districts generally, and particularly in those which border the Mediterranean. Many of the compounds of sulphur with the metals occur as natural productions in great abundance,—especially the sulphides of iron, copper, lead, and zinc. Bisulphide of iron (iron pyrites) furnishes a large proportion of the sulphur consumed in the manufacture of oil of vitriol. In the oxidized condition, as sulphuric acid, sulphur is still more extensively distributed in combination with various earths; the sulphates of lime, of magnesia, baryta, and strontia being abundant natural productions. Sulphur is also an essential constituent of many bodies of organic origin; it is, for example, always contained in the albuminoid or protein compounds.

*Properties.*—Native sulphur is found either in amorphous masses, or in transparent yellow octohedra with a rhombic base. The sulphur of commerce is either in the form of a harsh, yellow, gritty powder, known as *flowers of sulphur*, or in round sticks, constituting roll sulphur or common brimstone. In the latter condition it is a solid, nearly opaque, brittle substance, of a characteristic yellow colour, with a slight peculiar odour. It is insoluble in water, and is consequently tasteless: it is a bad conductor of heat, and when grasped with a warm hand frequently crackles and falls to pieces from the unequal expansion; it is an insulator of electricity, and becomes negatively electric by friction.

Sulphur is highly inflammable, and when heated in the air it takes fire between  $450^{\circ}$  and  $500^{\circ}$  F., burning with a blue flame, and emitting pungent suffocating fumes of sulphurous acid. At  $239^{\circ}$  F. it melts, forming a yellow liquid which is less dense than the undistilled sulphur. In close vessels it may, by a further heat, be distilled, the boiling point being about  $824^{\circ}$  F., according to the observation of Dumas; at this temperature sulphur yields a deep yellow vapour of sp. gr. 6.617: 1 volume of this vapour contains 3 equivalents of sulphur. Professor Graham states, on the authority of M. Bineau, that when sulphur is heated to about  $1800^{\circ}$  F. the

vapour becomes dilated to three times the bulk that should be produced by mere elevation of temperature, and that at this high temperature the volume occupied by an equivalent of sulphur vapour corresponds with that of an equivalent of oxygen.

*Extraction.*—Advantage is taken of the volatility of sulphur to purify it from the earthy matters which accompany it in its native state. A rough distillation is performed upon the spot where it is obtained. For this purpose a long brick furnace is constructed so as to contain a double row of upright earthenware retorts, each of a capacity of four or five gallons; these are furnished with a large aperture at the top for charging them with the sulphur, and with a short wide tube, which proceeds from the side at the upper part, and slopes downwards through the walls of the furnace into earthen receivers of a similar form: from the bottom of these receivers a short pipe carries off the still melted sulphur into vessels containing water. It is, however, still very impure, and requires a second more careful distillation before it is fit for many of the purposes to which it is applied in the arts. This second distillation is conducted in retorts, generally of iron, furnished with a short, wide, lateral neck; the fumes are received in large chambers of brick-work. If the walls of these chambers be kept cool, and the process be conducted slowly, the sulphur condenses in powder, and forms 'flowers of sulphur;' but if the fire be urged, and the masonry be allowed to become hot, the sulphur melts, runs down, and is then drawn off into cylindrical wooden moulds, which give it the usual form of roll sulphur.

When sulphur is prepared from pyrites ( $\text{FeS}_2$ ), the mineral is sometimes distilled in close vessels, and by this means about one-third of the sulphur which it contains is volatilized and condensed, magnetic pyrites,  $\text{Fe}_3\text{S}_4$ , remaining; but it is more usual to conduct the operation in the open air, as a preliminary step in the roasting of copper pyrites to prepare it for smelting. Huge heaps of the ore are arranged in the form of a truncated square pyramid, the base of which is about thirty feet in the side. A layer of powdered ore is placed at the bottom, and over this one of brushwood; in the centre is placed a wooden chimney, which communicates with air-ways left between the fagots; fragments of ore are now piled up until the heap is about eight feet high, and the whole is lastly covered, for a depth of twelve inches, with a layer of powdered ore. Such a heap contains upwards of 2000 tons of pyrites, and will furnish about twenty tons of sulphur. When the construction of the heap is complete, the fire is kindled in the centre by dropping lighted

—sagots down the chimney; in the course of a few days the heat becomes diffused throughout the mass, and sulphur begins to ooze from the surface. When this is observed, numerous hemispherical wells or excavations, fitted with covers, are made in the superficial layer of ore for the reception of the sulphur; into these cavities it drains, and is daily ladled out and cast into moulds. The process of roasting such a heap occupies five or six months.

(341) *Various forms of Sulphur.*—Sulphur has been already pointed out (84) as affording a striking illustration of the occurrence of allotropy: it may be obtained in several distinct modifications of form, or in different allotropic states.

The first form, which has been distinguished by the symbol  $S_a$ , is the native crystal of sulphur, the oblique rhombic octohedron. It may be obtained artificially by allowing the solution of sulphur, in chloride of sulphur, or in bisulphide of carbon, to evaporate spontaneously. It is semitransparent, of an amber yellow colour, and has a density of 2.05. Its crystals undergo no change in the air. They fuse at  $239^\circ \text{F}$ .

The second variety,  $S_\beta$ , is obtained by melting a few ~~pieces~~ of sulphur, and allowing it to solidify on the surface; if the crust be pierced with a hot wire, the still fluid portion may be poured off; and the solid mass beneath will be found to be lined with transparent brownish-yellow needles, belonging to the oblique prismatic form; these have a specific gravity considerably less than  $S_a$ , viz., 1.98, the density of ordinary roll sulphur. According to Mr. Brodie, it melts at  $248^\circ \text{F}$ . This form is not permanent in the air. In a few days, or (if the surface of the crystals be scratched) in a few hours, the transparency disappears, and although to the eye the crystals retain their prismatic outline, they lose their coherence, and an opaque crumbling mass is produced, consisting of minute rhombic octohedra. On the other hand, if an octohedron of  $S_a$  be placed in a liquid, the temperature of which is slowly raised to a point between  $220^\circ$  and  $230^\circ$ , it loses its transparency, owing to the formation of prismatic crystals.

The third variety,  $S_\gamma$ , is even more remarkable than the preceding: it is produced by the action of a still higher temperature. The influence of heat upon sulphur is indeed very peculiar. It begins to melt at about  $239^\circ$ , and between  $250^\circ$  and  $280^\circ$  it forms a yellow, transparent, and tolerably limpid liquid: as the temperature rises the colour deepens, it becomes brown, and at last nearly black and opaque. At  $350^\circ$  these changes are very decided; it gradually becomes more and more viscid; the temperature at this point for

awhile becomes stationary, notwithstanding continued accessions of heat from without, so that heat is becoming latent as in the analogous case of the melting of ice. After awhile, if the application of heat be steadily continued, the temperature again rises, and when it has attained to nearly  $500^{\circ}$  F., the sulphur once more liquefies, though it never becomes as fluid as at the temperature of  $240^{\circ}$  F. when first melted. If now suddenly cooled by pouring it in a slender stream into cold water, a soft tenacious mass is produced, which may be drawn out into elastic threads. The colour of the cooled threads varies from pale amber to a deep brown, becoming darker in proportion to the elevation of temperature it has experienced. Magnus has shown (Poggendorff's *Annal.*, xcii., 308) that this deepening in colour of the melted sulphur is due to the formation of another modification of sulphur, which is black; the more frequently the sulphur is heated up to about  $600^{\circ}$ , and then suddenly cooled, the larger is the quantity of this black sulphur which is formed. A red variety of sulphur was also obtained by Magnus: the details of the process required for insulating it in a state of purity are given at length in the memoir above referred to. Ductile sulphur has a sp. gr. of only 1.957. In a few hours it becomes yellow, and returns to the brittle form, giving out again the heat which it had absorbed; it also increases in density, the greater part of it assuming the form of  $S_{\alpha}$ . If this ductile sulphur be heated to  $212^{\circ}$ , it suddenly returns to the brittle condition, the temperature rising during the change to  $230^{\circ}$ .

Crystalline sulphur, either  $S_{\alpha}$  or  $S_{\beta}$ , dissolves freely in bisulphide of carbon, and in dichloride of sulphur: by spontaneous evaporation of the liquid, the sulphur is left in octohedra. Boiling oil of turpentine dissolves sulphur freely, and retains one and a half per cent. on cooling. As the liquid cools, the sulphur crystallizes, first in the prismatic form,  $S_{\beta}$ , afterwards as the temperature continues to fall, octohedra,  $S_{\alpha}$ , are produced. Vitreous sulphur,  $S_{\gamma}$ , is not soluble in bisulphide of carbon; after it has lost its vitreous and tenacious character it is not wholly changed into the ordinary form of sulphur, for it has become only partially soluble in bisulphide of carbon; a pale buff-coloured powder is left, soluble in anhydrous alcohol; it is of sp. gr. 1.955, and it may, by fusion, be reconverted into ordinary sulphur, which is soluble in bisulphide of carbon. The black sulphur of Magnus is also insoluble in bisulphide of carbon.

When distilled in small quantities, in vessels in which the

temperature is not considerably reduced in the receiver, the sulphur condenses in red drops, which remain liquid for many hours. Sulphur is also frequently liberated in the ductile form from the native sulphides of the metals during their solution in *agua regia*.

(342) COMPOUNDS OF SULPHUR WITH OXYGEN. — Sulphur forms numerous compounds with oxygen: two of them (sulphurous acid and sulphuric acid) have been long known and employed on a large scale in the arts; the others are less important, and of comparatively recent discovery. These acids of sulphur are interesting, as they exhibit a combining ratio different from any that has as yet been considered, and they show the application of the law of multiple proportions to the case of the sulphur, as well as to that of the oxygen which they contain.

The following table exhibits the composition of the various combinations of sulphur with oxygen, the existence of which is at present known:—

$\text{SO}_2$	Sulphurous acid
$\text{SO}_3$	Sulphuric acid
$\text{S}_2\text{O}_2$	Dithionous or hyposulphurous acid.
$\text{S}_2\text{O}_5$	Dithionic or hyposulphuric acid
$\text{S}_3\text{O}_5$	Tritbionic acid
$\text{S}_4\text{O}_5$	Tetrathionic acid
$\text{S}_5\text{O}_5$	Pentathionic acid.

We will examine first the sulphurous acid, then the sulphuric acid, and will pass slightly over the other acids, the compounds of which, with the exception of some of the salts of hyposulphurous acid, have as yet received no practical applications.

(343) SULPHUROUS ACID, ( $\text{SO}_2$ ); *Equivalent*, 32; *Combining Volume*, 2; *Specific Gravity*, 2.247.—Sulphur burns in oxygen with a rose-coloured flame, and produces a permanent gas; after the combustion has terminated, and the gas has been allowed to regain its original temperature, the bulk of the gaseous products is found to be the same as before the experiment. Sulphurous acid is the sole product of the combination if the oxygen be dry. This gas is endowed with the properties of a weak acid; it has a pungent, suffocating odour, like that of burning sulphur, and in a concentrated form it is quite irrespirable. It is not inflammable, but quickly extinguishes the flame of burning bodies. Sulphurous acid dissolves freely in water, which takes up between forty and fifty times its bulk of the gas; the liquid has a taste and smell similar to that of the gas; the solution gradually absorbs oxygen from the air, and becomes con-

verted into sulphuric acid ( $\text{SO}_3$ ). A crystalline hydrate of sulphurous acid ( $\text{SO}_2 \cdot 9 \text{HO}$ ) may also be obtained at a low temperature; at  $40^\circ \text{F}$ . this hydrate melts and is decomposed. Owing to the solubility of sulphurous acid in water, the gas must always be collected either over mercury, or in dry bottles by displacement: from the high density of the gas (double that of oxygen), the latter method is easily applied.

*Preparation.*—When required in a pure state, sulphurous acid is always prepared by depriving oil of vitriol of part of its oxygen. In order to effect this, two or three ounces of sulphuric acid in a concentrated form may be boiled in a glass retort upon half an ounce of copper or of mercury. Part of the acid gives up 1 equivalent of its oxygen to the metal; the oxide thus produced combines with an equivalent of the undecomposed acid, whilst an equivalent of sulphurous acid is set free for each equivalent of the sulphate formed. The reaction in the case of copper may be seen in the following equation:  $\text{Cu} + 2 \text{SO}_3 = \text{CuO}, \text{SO}_3 + \text{SO}_2$ . The gas must be washed by allowing it to bubble up through a bottle containing a small quantity of water, which retains sulphuric acid and any impurities which might be mechanically suspended in the gas. According to Maumené, a certain quantity of the disulphide of copper,  $\text{Cu}_2\text{S}$ , is also produced during this operation, after which a mixture of sulphide and oxysulphide of copper is also formed. Sulphuric acid may be more economically deoxidized by means of charcoal or dry saw-dust, but the gas in this case is accompanied by one half its volume of carbonic acid;  $\text{C} + 2 \text{SO}_3$  gives  $\text{CO}_2 + 2 \text{SO}_2$ . For most purposes, however, such as the preparation of the alkaline sulphites, the presence of carbonic acid is unimportant. Sulphurous acid may also be readily procured by heating in a flask an intimate mixture of 4 parts of flowers of sulphur and 5 of finely powdered peroxide of manganese;  $\text{S}_2 + \text{MnO}_2 = \text{SO}_2 + \text{MnS}$ .

By transmitting sulphurous acid gas through a tube surrounded by a mixture of ice and salt, sulphurous acid may be condensed to a colourless, transparent, limpid liquid, of specific gravity 1.42, which dissolves bitumen; this liquid boils at  $17^\circ.6$ , and freezes at  $-105^\circ \text{F}$ ., forming a transparent, colourless, crystalline solid, heavier than the liquid; in closed tubes, at  $60^\circ$  it exerts a pressure of about two atmospheres and a half (Faraday).

Fig. 261 shows a method of liquefying sulphurous acid. The gas is generated in the flask, A, washed and dried by means of concentrated sulphuric acid placed in the bottle, B, transmitted through the pewter worm, C, surrounded by a freezing mixture of ice and



salt, and collected in the receiver, D, which is also cooled by a freezing mixture; the liquefied acid is stored up for use in small

FIG. 261.

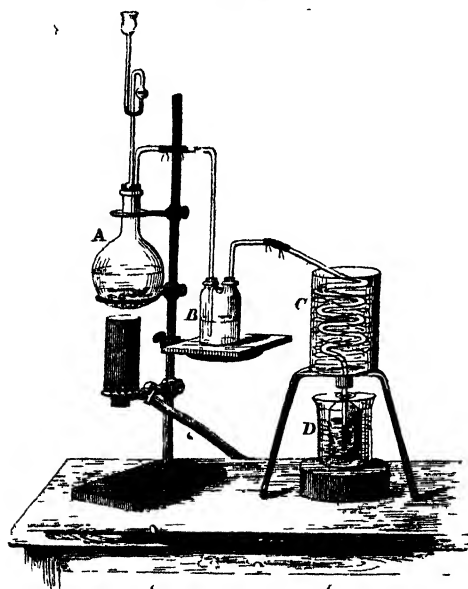


FIG. 262.



tubes, one of which is shown at E, fig. 262; the tube having been previously cooled by immersion in the freezing mixture, the acid is poured into it through a small tube funnel, and the liquid is preserved by drawing off and sealing the tube at the narrow portion in the flame of the blowpipe, whilst the receiver still remains in the freezing mixture.

Sulphurous acid possesses considerable bleaching powers, and is extensively employed in bleaching straw and wool. The articles to be bleached are moistened and suspended in closed chambers in which sulphur is burned in an open dish; the sulphurous acid is absorbed by the damp goods, and the colour is discharged. The gas appears to act by forming colourless compounds with certain colouring matters. It does not, like chlorine, decompose the colouring matter; for the sulphurous acid may either be expelled by a stronger acid, or it may be neutralized by an alkali, and the colour will be restored: the reproduction of the yellow colour in new flannel, when it is washed with an alkaline soap for the first time, is a practical illustration of the effect of an alkali upon goods which have been bleached by sulphurous acid. Sulphurous acid is also highly valuable as a disinfecting agent.

It is, however, principally as a preliminary step in the manufacture of oil of vitriol that sulphurous acid is made upon the large scale, and in this case it is always obtained by burning sulphur, or a metallic sulphide, in air.

The composition of sulphurous acid is easily determined synthetically, by simply burning sulphur in oxygen; the bulk of the gas is not increased, but the density of the sulphurous acid is double that of oxygen. Equal weights of sulphur and oxygen, it is therefore clear, must have united to produce the result.

*Sulphites.*—Sulphurous acid is a weak acid, and presents considerable analogy to carbonic acid in its mode of combining with bases; and according to Dr. Muspratt's observation, the sulphites and the carbonates are in many cases isomorphous. With the alkalies it forms two kinds of salts, one of which, like the ordinary sulphite of soda ( $\text{NaO}, \text{SO}_2, 10 \text{ aq}$ ), contains 1 equivalent of the acid to 1 of alkali, while the other class, represented by the bisulphite of potash ( $\text{KO}, \text{HIO}, 2 \text{ SO}_2$ ), contains 2 equivalents of acid to 1 of base. The sulphites of the alkalies are the only ones which dissolve freely in water; but those of baryta, strontia, and lime, dissolve to some extent in an aqueous solution of sulphurous acid. By a strong heat many of the sulphites are decomposed, the acid being gradually expelled. They are also decomposed by sulphuric or hydrochloric acid, with extrication of sulphurous acid, which is known by its peculiar and pungent odour. The best test for detecting small traces of sulphites consists in the addition of a fragment of zinc and a drop or two of hydrochloric acid to the solution; the sulphurous acid is deoxidized, the sulphur combines with hydrogen, and sulphuretted hydrogen is given off; the gas last named may be detected by suspending a piece of paper moistened with solution of acetate of lead in the upper part of the vessel, which should be closed by a glass plate. The sulphites, when moist, absorb oxygen from the air; and solutions of the salts are often used as deoxidizing agents: for example, the salts of sesquioxide of iron are reduced to salts of the protoxide. Gold, selenium, and tellurium, are precipitated by them from their solutions in hydrochloric acid in the reduced or metallic form, and arsenic acid is reduced to arsenious acid.

The sulphites are readily formed by transmitting a stream of sulphurous acid through water in which the oxide or the carbonate of the metal is dissolved or suspended, the carbonates being decomposed with effervescence.

Sulphurous acid is by some chemists regarded as the starting point of several combinations belonging to the sulphur series.

Without attaching much importance to the probability of this view, we subjoin the following table, which exhibits the supposed relation of some of the more important of these compounds to sulphurous acid :—

Sulphurous acid,	$\text{SO}_2$	
Sulphuric acid,	$\text{SO}_2 \text{ O}$ ,	oxide of sulphurous acid.
Chlorosulphuric acid,	$\text{SO}_2 \text{ Cl}$ ,	chloride of ditto.
Iodosulphuric acid,	$\text{SO}_2 \text{ I}$ ,	iodide of ditto.
Nitrosulphuric acid,	$\text{SO}_2 \text{ NO}_2$	
Hyposulphurous acid,	$\text{SO}_2 \text{ S}$ ,	sulphide of ditto.

(344) SULPHURIC ACID, ( $\text{SO}_3$ ); *Equivalent*, 40; *Combining Volume of Vapour*, 2; *Specific Gravity of Vapour*, 2.763.—This substance, which for commercial purposes is one of the most important products of chemical manufacture, is made in enormous quantities. In Great Britain alone upwards of 100,000 tons are annually consumed.

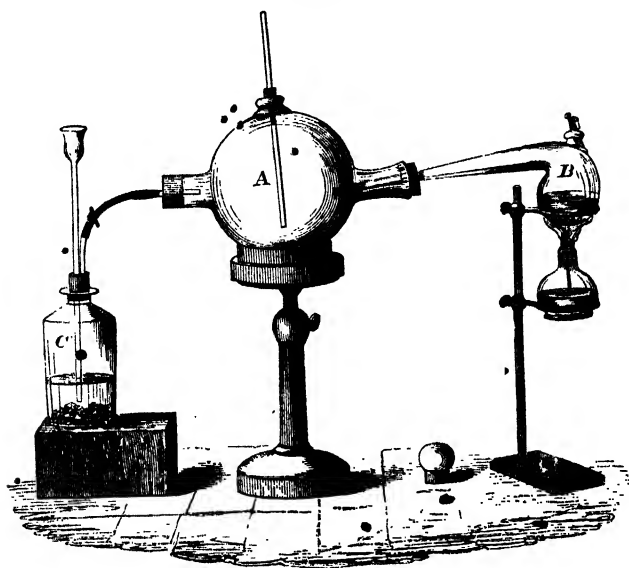
*Preparation.*—When sulphur is boiled in *aqua regia*, or in concentrated nitric acid, it is gradually oxidized and converted into sulphuric acid; but this method is never employed excepting for experimental purposes in the laboratory. On the large scale it is made by a process first employed in England by Dr. Roebuck, and introduced about the year 1720, since which period the mode of conducting it has undergone several modifications and improvements, though in principle it continues to be the same.

The changes which occur in the process are remarkable and instructive. It has been already mentioned, that when sulphur is burned in air or oxygen, the product is sulphurous acid; this gas, if made to combine with half as much oxygen again as it already contains, is converted into sulphuric acid. Direct combination, however, cannot be produced between the two gases; the intervention of some third substance becomes necessary; and if water be presented to them, a very gradual process of oxidation occurs. If pure and dry oxygen, mixed with twice its bulk of sulphurous acid, be transmitted over spongy platinum (62) heated in a tube, the two gases combine, and anhydrous sulphuric acid ( $\text{SO}_3$ ) is produced.

If sulphurous acid mixed with oxygen be presented to deutoxide of nitrogen, or to any other of the higher oxides of nitrogen, this combination may however be effected with great rapidity; and further, a very small proportion of the deutoxide of nitrogen will suffice to effect the combination of an almost indefinite amount of sulphurous acid and oxygen, if water be also present. Upon these

facts the process employed in the manufacture of sulphuric acid is founded. The reaction is easily watched upon the small scale by the following means:—Into a large three-necked receiver, A, fig. 263, filled with atmospheric air, and slightly moistened in the

FIG. 263.

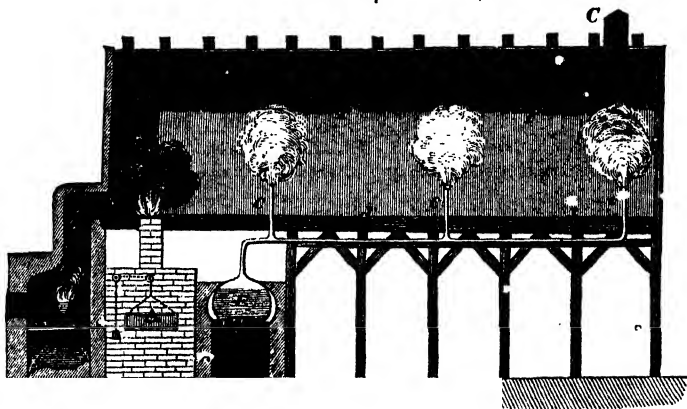


interior, sulphurous acid from the retort, B, and deutoxide of nitrogen from the bottle, C, are made to pass; ruddy fumes of peroxide of nitrogen are immediately formed by the combination of the deutoxide with atmospheric oxygen, and in a few minutes the inner surface of the receiver becomes coated with a white crystalline deposit, into the composition of which sulphurous acid, peroxide of nitrogen, and water enter. As soon as this crystalline mass is treated with water, it is decomposed with brisk effervescence; 1 equivalent of deutoxide of nitrogen escapes, and 2 equivalents of sulphuric acid remain in solution: the deutoxide of nitrogen, by again absorbing 2 equivalents of oxygen from the air, is reconverted into peroxide of nitrogen; this combines again with two fresh equivalents of sulphurous acid in the presence of a small quantity of water; fresh crystals are formed, and these in their turn are decomposed by solution, as before. The deutoxide of nitrogen is thus again liberated, and may go through the same round of compositions and decompositions, till the whole of the oxygen in the air has been consumed: the oxide of nitrogen thus

acts the part of a carrier of oxygen to the sulphuric acid. In the manufacture of sulphuric acid on the large scale, the formation of the crystalline body and its destruction are simultaneous, if the operation be properly conducted.\*

(345) In the manufacture of sulphuric acid, sulphurous acid is procured by burning either sulphur or iron pyrites ( $\text{FeS}_2$ ); provision being made for an abundant supply of atmospheric air to the burning material. The general arrangements adopted in the manufacture, are shown in fig. 264. A A, represent fur-

FIG. 264.



naces in which the sulphur is burned; in the current of heated gas an iron pot, *b*, is suspended, which has been previously charged with a mixture of nitrate of soda and oil of vitriol.

\* The true composition of this crystalline body has been the object of much discussion and numerous experimental inquiries. H. Rose has shown that by passing pure dry binoxide of nitrogen into a glass vessel, the interior of which is moistened with anhydrous sulphuric acid ( $\text{SO}_3$ ), a white, hard, amorphous substance is formed, composed of  $(\text{NO}_2 \cdot 2 \text{SO}_3)$ , and this compound he considers to be the essential constituent in the crystals above described. It fuses at a high temperature, and sublimes unchanged. Water immediately decomposes it, liberating deutoxide of nitrogen whilst the sulphuric acid is dissolved. If the anhydrous crystals be exposed to the air, they absorb moisture and emit nitrous fumes. Concentrated oil of vitriol, by the aid of heat, dissolves them in all proportions without change. The solution crystallizes, on cooling, in rectangular prisms, which appear to contain water of crystallization.

Oil of vitriol rapidly absorbs the deutoxide of nitrogen, and forms a similar crystalline compound; the addition of water immediately liberates the deutoxide of nitrogen from it.

There are many other methods by which this curious substance may be obtained, but they often involve very complicated considerations. De la Provostaye forms it by the action of liquid sulphurous acid on liquid peroxide of nitrogen; he considers it when anhydrous to consist of  $\text{SO}_3 + \text{SO}_2 + \text{NO}$ . Rose's view however is more probably correct.

Vapours of nitric acid are thus liberated; they pass on with the sulphurous acid, by suitable flues, into immense chambers, F, F, constructed of sheet lead, and supported by a strong timber framework. These chambers are often twelve or fifteen-feet high, fifteen or twenty wide, and from 150 to 300 feet in length; they are sometimes partially intersected by incomplete transverse leaden partitions, interposed in the current of the mixed gases, to favour their more intimate admixture. Water to the depth of two or three inches is placed upon the floor of the chamber, d, d, to condense the acid; and the mutual re-action of the atmospheric oxygen, sulphurous acid, and deutoxide of nitrogen is further facilitated by the injection of jets of steam, c, c, c, supplied from the boiler, E. The nitric acid extricated from the nitre, speedily becomes de-oxidized by the sulphurous acid to the state of deutoxide of nitrogen, and then the changes already pointed out, rapidly succeed each other, and sulphuric acid is formed in large quantity.

In a properly managed chamber, the gases which pass off by the exit-flue, c, consist only of nitrogen and deutoxide of nitrogen, the sulphurous acid and oxygen being supplied just in sufficient quantities mutually to condense each other, fresh atmospheric air entering at the other end along with the sulphurous acid.

M. Gay Lussac has taken advantage of the solubility of deutoxide of nitrogen in oil of vitriol, to economise the consumption of nitre in the process, which upon the old plan, amounts to from one-eighth to one-twelfth of the weight of the sulphur consumed. By the contrivance to be mentioned immediately, the quantity of nitre formerly requisite has been reduced by one-half. The improvement consists in conducting the spent gases into a leaden tower filled with fragments of coke, through which a stream of concentrated sulphuric acid is continually trickling. The acid thus becomes charged with the nitrous vapours, and flows off at the bottom of the tower to a reservoir from which it is again raised by a forcing pump to the top of a second similar tower at the entrance of the chamber, where it is deprived of the nitrous compounds by the sulphurous acid gas as it enters from the furnace. This plan has not as yet come into general use in this country.

The sulphuric acid which collects at the bottom of the chambers is in too dilute a condition for sale: it is not found advantageous to allow it to attain a greater degree of concentration than 1.45 in the chambers, as it becomes liable to absorb and retain the nitrous fumes. When it has reached a specific gravity of about 1.45, it is drawn off and evaporated in shallow leaden.

pans till it has acquired a density of 1·720; beyond this point the concentration cannot be carried in these vessels, as the temperature required would endanger the melting of the leaden pan, and its corrosion by the acid. The liquid is therefore drawn off into glass retorts, or, as is now practised in many works with great advantage, into platinum stills; in these it is again further heated until white fumes of oil of vitriol pass over. Beyond this point it is useless to carry the operation, as the concentrated acid distils over. Indeed during the whole operation, some acid passes over with the water, which is therefore preserved, and returned to the leaden chamber.

The acid that remains in the retort after it has been thus boiled down, is the concentrated oil of vitriol of commerce—it is a definite hydrate of sulphuric acid, containing 1 equivalent of acid and 1 of water ( $\text{HO}, \text{SO}_3$ )\*

The following table, according to Dr. Ure, gives the proportion of sulphuric acid contained in solutions of the densities therein mentioned at 60° F.

*Strength of Sulphuric Acid of Different Densities.*

Specific Gravity,	SO <sub>3</sub> in 100 parts,	HO, SO <sub>3</sub> .	Specific Gravity,	SO <sub>3</sub> in 100 parts,	HO, SO <sub>3</sub> .	Specific Gravity,	SO <sub>3</sub> in 100 parts,	HO, SO <sub>3</sub> .
1·8460	81·54	100	1·5503	53·82	66	1·2334	26·09	32
1·8415	79·90	98	1·5280	52·18	64	1·2184	24·46	30
1·8366	78·28	96	1·5066	50·55	62	1·2032	22·83	28
1·8288	76·65	94	1·4860	48·92	60	1·1876	21·20	26
1·8181	75·02	92	1·4660	47·29	58	1·1706	19·57	24
1·8070	73·39	90	1·4460	45·66	56	1·1549	17·94	22
1·7901	71·75	88	1·4265	44·03	54	1·1410	16·31	20
1·7728	70·12	86	1·4073	42·40	52	1·1246	14·68	18
1·7540	68·49	84	1·3884	40·77	50	1·1090	13·05	16
1·7315	66·86	82	1·3697	39·14	48	1·0953	11·41	14
1·7080	65·23	80	1·3530	37·51	46	1·0809	9·78	12
1·6860	63·60	78	1·3345	35·88	44	1·0682	8·15	10
1·6624	61·97	76	1·3165	34·25	42	1·0544	6·52	8
1·6415	60·34	74	1·2999	32·61	40	1·0405	4·89	6
1·6204	58·71	72	1·2826	30·98	38	1·0268	3·26	4
1·5975	57·08	70	1·2654	29·35	36	1·0140	1·65	2
1·5760	55·45	68	1·2490	27·72	34	1·0074	0·815	1

(346) *Hydrates of Sulphuric Acid.*—The oil of vitriol of commerce forms a dense, oily looking colourless liquid, without smell, and of specific gravity 1·842. It is intensely caustic, and chars almost

\* Marignac (*Ann. de Chimie*, III. xxxix, 189) finds that it always contains a slight excess of water beyond the atomic proportion; instead of 18·36 per cent. of water, he always obtained 19·62.

all organic substances, from its powerful affinity for moisture. With water it mixes completely in all proportions; great heat is given out at the moment the mixture is made, and the mixture, when cold, occupies less bulk than the two liquids did when separate. The dilution should therefore be performed gradually, always pouring the acid into the water, not the water into the acid. So powerful is the attraction of the acid for moisture, that if exposed in a shallow dish to the air for a few days, it frequently doubles its weight by absorbing aqueous vapour from the air. The acid of commerce is often of a dark brown colour, occasioned by its charring action on fragments of organic matter, such as straw or wood, which have accidentally fallen into it. Sulphuric acid does not evaporate at the ordinary temperature of the air. If a drop of dilute acid fall upon a cloth, the water gradually evaporates until the acid which is left behind acquires a considerable degree of concentration. On approaching a fire or other source of heat, a further portion of the water is expelled, and the acid becomes more concentrated, till it chars or destroys the cohesion of the fibres—hence the destructive action of sulphuric acid upon linen, even when very much diluted.

Marignac finds that the true monohydrate of sulphuric acid when heated emits a small quantity of the vapour of the anhydrous acid, and the remaining liquid boils at  $640^{\circ}$  F. After it has been frozen, it melts at  $51^{\circ}$ , but it may be cooled much below this point without solidifying. On dropping into the cooled acid a crystal of the acid previously frozen, congelation immediately occurs, and the temperature rises to  $51^{\circ}$  F. The concentrated acid of commerce does not usually freeze till it has been cooled to about  $-30^{\circ}$  F.

*Bihydrate of Sulphuric Acid*, ( $\text{HO}, \text{SO}_3 + \text{HO}$ ).—If water be added to sulphuric acid, until the density is reduced to 1.78, a second hydrate, which contains 2 equivalents of water, is formed. It freezes at  $47^{\circ}$ , and crystallizes in splendid rhombic prisms; from this property it is often termed glacial sulphuric acid. According to Dalton, it boils at  $435^{\circ}$ . Mr. Graham found that this hydrate may be obtained by heating a more dilute acid to  $400^{\circ}$  F. till it ceases to give off water.

A *terhydrate* ( $\text{HO}, \text{SO}_3 + 2\text{HO}$ ) may, according to Mr. Graham, be procured by evaporating a dilute acid *in vacuo* at  $212^{\circ}$ , till it ceases to lose weight. The density of this hydrate is 1.632, and its boiling point is  $348^{\circ}$ .

*Nordhausen Sulphuric Acid*.—For the purpose of dissolving indigo in the process of dyeing Saxony blue, an acid of still higher



concentration than oil of vitriol is required. Such an acid is principally prepared at the town of Nordhausen, in Saxony, and is hence known as Nordhausen oil of vitriol: in preparing it, sulphate of iron is dried at a moderate heat to expel its water of crystallization, and is then distilled in earthen retorts; a dense, brown, fuming liquid passes over, of sp. gr. about 1.9.

*Anhydrous Sulphuric Acid*, ( $\text{SO}_3$ ).—If this fuming Nordhausen acid be placed in a glass retort, furnished with a receiver which is kept cool by ice, and a gentle heat be applied to the retort, white fumes pass over, which condense into a white silky-looking fibrous mass. This is the compound of 1 equivalent of sulphur with 3 of oxygen, commonly called anhydrous sulphuric acid. The remainder in the retort, after all the anhydrous acid is expelled, consists of ordinary oil of vitriol. Anhydrous sulphuric acid may also be obtained from the bisulphate of soda ( $\text{NaO}, \text{HO}, 2 \text{SO}_3$ ), which melts at a dull red heat, and is deprived of its equivalent of water; when distilled in an earthen retort, it yields white fumes of the anhydrous acid, whilst neutral sulphate of soda ( $\text{NaO}, \text{SO}_3$ ) remains in the retort. Combined with 1 equivalent of oil of vitriol it crystallizes in plates consisting of  $2 \text{SO}_3, \text{HO}$ .

The so called anhydrous sulphuric acid, however, in this state possesses no acid properties. It is tough, ductile, and can be moulded in the fingers, like wax, without charring the skin. It fumes in the air, and is very deliquescent; when thrown into water it hisses as a hot iron would do from the heat emitted. The solution has all the properties of ordinary sulphuric acid. The anhydrous compound melts at  $65^\circ \text{F}$ ., and boils at about  $110^\circ$ , forming a colourless vapour, which if passed through ignited porcelain tubes is decomposed into 2 volumes of sulphurous acid and 1 volume of oxygen; 1 volume of sulphur vapour and 3 volumes of oxygen are condensed into 2. The specific gravity of this vapour is 2.763. According to Marignac, anhydrous sulphuric acid exists under two modifications; one of which melts about  $65^\circ \text{F}$ ., and is produced by distillation, or by fusion at a high temperature; but when once it has been solidified, it passes rapidly into the other form, which melts near  $212^\circ \text{F}$ ., at which temperature it slowly volatilizes, and is reconverted into the first variety.

Anhydrous sulphuric acid combines with sulphur, forming solutions which have a brown, green, or blue colour, according to the proportion of sulphur; the blue compound containing the smallest proportion. It also dissolves iodine, and with one-tenth of its weight of iodine forms a green crystalline compound.

We are, therefore, acquainted with the following definite compounds of sulphuric acid with water; starting with the anhydrous acid :—

		Fusing point ° F.	Boiling point ° F.	Specific gravity.
Anhydrous	$\text{SO}_3$	65		
Dihydrate	$\text{HO}, 2 \text{SO}_3$	95		
Monohydrate	$\text{HO}, \text{SO}_3$	51	640	1.842
Bihydrate	$2 \text{HO}, \text{SO}_3$	77	435	1.780
Terhydrate	$3 \text{HO}, \text{SO}_3$		348	1.632

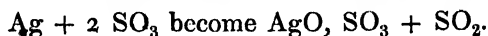
The applications of sulphuric acid in the arts are very numerous. Immense quantities of it are consumed in the manufacture of sulphate of soda as a preliminary process in making carbonate of soda; and it is in constant requisition for the preparation of nitric, hydrochloric, and other volatile acids. In the laboratory its applications are too numerous to be specified.

(347) *Impurities common in the Commercial Acid.*—The oil of vitriol of commerce is never pure; it always contains lead, derived from the vessels in which it is made. The sulphate of lead is precipitated as a white powder when the acid is diluted. It is also frequently contaminated with arsenic, derived from the pyrites: the diluted acid in this case gives a yellow precipitate when exposed to a current of sulphuretted hydrogen gas. The arsenic is still more easily recognised by what is termed Marsh's test, which will be described under the head of arsenic. Nitric acid, and some of the lower oxides of nitrogen, are also often present. A strong solution of green vitriol in water, when added to the undiluted acid, shows the presence of these impurities by striking a characteristic purplish-red colour at the point of contact of the two liquids. Sulphurous acid may likewise sometimes be detected in the acid, as may also hydrochloric acid and sulphate of potash.

When required pure, the acid must be re-distilled with a little sulphate of ammonia; this salt decomposes any nitrous acid which may be present (p. 514). The distillation requires to be conducted with much care, as the boiling takes place with violent concussions and sudden bursts of vapour: the best plan for avoiding danger, consists in applying heat to the sides, and not to the bottom of the retort; this may be effected by using a gas-burner in the form of a large ring. The insoluble matters collect at the bottom of the retort, whilst the ebullition takes place from the sides tranquilly.

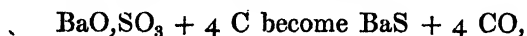
In its concentrated form sulphuric acid acts but feebly

upon metallic bodies in the cold, but when boiled upon them it in some cases undergoes decomposition: even silver is dissolved by it; the metal is oxidized at the expense of a part of the oxygen of the acid, sulphurous acid being formed, whilst the sulphate of the metal dissolves in the excess of sulphuric acid: thus



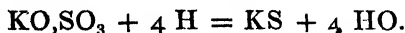
Copper, mercury, antimony, bismuth, lead, and tellurium act upon the acid in a similar manner. Gold, platinum, rhodium, and iridium are not acted upon by the acid even when boiled with it. The more oxidizable metals are dissolved by this acid when diluted with water, water being decomposed and hydrogen liberated, whilst the oxygen of the water combines with the metal, and the metallic oxide at the moment of its formation unites with the sulphuric acid: zinc, iron, cobalt, nickel, and manganese, are acted upon in this way.

*Sulphates.*—The sulphates are for the most part composed of 1 equivalent of acid and 1 of metallic oxide, like sulphate of zinc ( $\text{ZnO}, \text{SO}_3$ ). There are, however, strong grounds for believing that sulphuric acid is what is termed a bibasic acid (460). With the alkalis it forms acid salts, such as bisulphate of potash ( $\text{HIO}, \text{KO}, 2 \text{SO}_3$ ), and in a few instances basic salts, such as the subsulphate of copper ( $3 \text{CuO}, \text{SO}_3 + 2 \text{aq}$ ), are formed. The sulphates of the alkalis and of the alkaline earths are not decomposed when heated to redness: the sulphates of zinc, cadmium, nickel, cobalt, copper, and silver require an intense heat to decompose them; but the other sulphates part with their acid without difficulty when strongly ignited. When heated with charcoal the sulphates are all decomposed; those of the alkalis and alkaline earths being converted into sulphides: the residue, when moistened with hydrochloric acid, evolves sulphuretted hydrogen. Thus sulphate of baryta may be easily recognised even in small quantity, if, after having been mixed with a little charcoal and folded in a piece of platinum foil, it is heated in the flame of the blowpipe:



the carbonic oxide escapes as gas, and the sulphide of barium, when moistened with hydrochloric acid, becomes chloride, evolving hydrosulphuric acid;  $\text{BaS} + \text{HCl} = \text{BaCl} + \text{HS}$ . The sulphates of the alkalis and alkaline earths may also be converted into sulphides by heating them to redness in a glass or porcelain tube, and transmitting a current of dry hydrogen gas over them.

In this way sulphate of potash is easily reduced to sulphide of potassium, water being formed: thus.



Sulphuric acid and its salts are easily recognised when in solution by the white precipitate which occurs on the addition of nitrate of baryta; this precipitate is insoluble in nitric acid. A white precipitate of sulphate of lead, nearly as insoluble as the sulphate of baryta, is formed on adding a soluble salt of lead to a solution containing sulphuric acid or a sulphate. The sulphates of strontia, lime, and silver are but sparingly soluble in water; the others dissolve readily; nearly all the sulphates are insoluble in alcohol, unless a large excess of acid be present.

(348) HYPOSULPHUROUS ACID, ( $\text{S}_2\text{O}_2$ ); *Equivalent*, 48.—Of the remaining acids of sulphur, the only one of any practical importance is the hyposulphurous or *dithionous* acid. In combination with soda it has been largely employed in the fixing of photographic pictures. This application has arisen from its power of dissolving those salts of silver which are insoluble in water, forming with them soluble double salts; the surface of the photograph is freed from the unaltered argentine compounds by immersion in a solution of the hyposulphite; after which, if well washed with water, it is no longer liable to alteration by exposure to light.

If zinc filings be digested in a solution of sulphurous acid, the metal dissolves without any extrication of gas, it is oxidized at the expense of a portion of the sulphurous acid, and a mixture of sulphite and hyposulphite of zinc is found in solution ( $3 \text{SO}_2 + 2 \text{Zn} = \text{ZnO},\text{S}_2\text{O}_2 + \text{ZnO},\text{SO}_2$ ). No practical applications have been made of the hyposulphite of zinc. The hyposulphite of soda is manufactured to some extent by transmitting through a solution of impure sulphide of sodium (prepared by fusing together in a covered crucible equal weights of carbonate of soda and flowers of sulphur) a stream of sulphurous acid until it ceases to be absorbed; the liquid is then filtered and evaporated; hyposulphite of soda ( $\text{NaO},\text{S}_2\text{O}_2 + 5 \text{aq}$ ) crystallizes from the solution in bold striated rhombic prisms, terminated by oblique faces. A still better plan consists in digesting a solution of sulphite of soda on powdered sulphur. The sulphur gradually dissolves and forms a colourless solution, which on evaporation yields crystals of hyposulphite of soda, 1 equivalent of sulphur combining with 1 equivalent of sulphite of soda;  $\text{NaO}, \text{SO}_2 + \text{S}$  give  $\text{NaO}, \text{S}_2\text{O}_2$ . A hyposulphite of baryta may be obtained in small

brilliant crystals by mixing dilute solutions of chloride of barium and hyposulphite of soda.

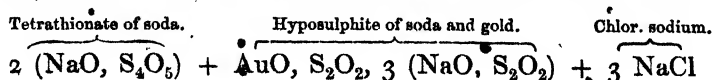
It is impossible, however, to obtain the acid in an insulated form either from this or from any of its salts; when, for example, sulphuric acid is added to the hyposulphite of baryta, sulphate of baryta is precipitated, but if the solution be filtered, the clear liquid speedily becomes milky from the separation of sulphur, and the odour of sulphurous acid is emitted;  $S_2O_2$  becomes  $S + SO_2$ .

The soluble hyposulphites are easily recognised by the facility with which they dissolve chloride of silver, forming a solution of an intensely sweet taste.  $AgCl + 2 (NaO, S_2O_2) = NaCl + NaO, AgO, 2 S_2O_2$ .

They give a brown precipitate, consisting of sulphide of copper, when heated with a solution of a salt of copper acidulated with hydrochloric acid; and a white precipitate of hyposulphite of lead in solutions of the salts of lead; this precipitate, however, becomes decomposed and blackened if dried at  $212^\circ$ , owing to its partial conversion into sulphide of lead: nitrate of suboxide of mercury is decomposed immediately at ordinary temperatures in a similar manner, the black sulphide of mercury being deposited. An alcoholic solution of iodine is rendered colourless by admixture with an excess of hyposulphite; a tetrathionate of the base being produced (351).

When heated in close vessels the hyposulphite of soda loses water, and then is resolved into sulphate of soda and pentasulphide of sodium.  $4 (NaO, S_2O_2) = 3 (NaO, SO_3) + NaS_5$ . Solutions of the hyposulphites of lime and strontia are decomposed below the temperature of  $212^\circ$  into free sulphur and sulphites of the earths.

MM. Fordos and Gélis (*Ann. de Chimie*, III., xiii., 399) have shown that hyposulphite of soda, when mixed with chloride of gold, forms chloride of sodium, tetrathionate of soda ( $NaO, S_4O_6$ ), and a double hyposulphite of soda and oxide of gold; ( $AuO, S_2O_2 + 3 (NaO, S_2O_2) + 4 aq$ ). The latter salt is used for gilding the daguerreotype plate, and for colouring the positive proof obtained in photographic printing. The formation of this double salt admits of explanation by the following equation:  $8 (NaO, S_2O_2) + AuCl_3 =$



The double hyposulphite of soda and gold may be obtained in a state of purity by mixing concentrated solutions of 1 part of chloride of gold and 3 parts of hyposulphite of soda: on the addition of

alcohol it is precipitated; the precipitate must be redissolved in a small quantity of water, and again precipitated by alcohol.

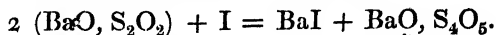
(349) **HYPOSULPHURIC ACID**: *Dithionic Acid*, ( $S_2O_5$ ); *Equivalent*, 72. — This acid is more stable than the hyposulphurous acid, and may be obtained in combination with water. If sulphurous acid be transmitted through water in which finely divided peroxide of manganese is suspended, the gas is rapidly absorbed, and if the liquid be kept cool, hyposulphate of manganese is formed,  $MnO_2 + 2 SO_2 = MnO, S_2O_5$ . If the temperature be allowed to rise, sulphate of manganese is formed instead,  $MnO_2 + SO_2 = MnO, SO_3$ . It is difficult to prevent the formation of a little of the latter salt, but the two salts are easily separated; by adding baryta water the protoxide of manganese is precipitated, and sulphate and hyposulphate of baryta are formed ( $MnO, SO_3 + MnO S_2O_5 + 2 BaO = BaO, SO_3 + BaO S_2O_5 + 2 MnO$ ). The hyposulphate of baryta, being soluble, may be separated from the insoluble sulphate of baryta by filtration, and by the cautious addition of dilute sulphuric acid to the filtered liquid, until a precipitate ceases to form on the addition of a drop of sulphuric acid, hyposulphuric acid may be liberated and filtered from the additional sulphate of baryta.

When heated, the hyposulphates give off sulphurous acid and a sulphate of the base remains behind. The hyposulphates are all soluble in water. At a boiling heat they may be oxidized by chlorine or by nitric acid, and two equivalents of sulphuric acid are formed,  $S_2O_5 = O + 2 SO_3$ . In the cold, they present no appearance of decomposition when treated with sulphuric acid, but if heated with it, sulphurous acid is evolved, but no deposit of sulphur occurs. These reactions distinguish the hyposulphates from both the sulphites and the hyposulphites.

(350) **TRITHIONIC ACID**, ( $S_3O_6$ ); *Equivalent*, 88. — If a saturated solution of bisulphite of potash be digested on flowers of sulphur for three or four days, till the yellow colour has disappeared, sulphurous acid gradually escapes and trithionate of potash is formed. It crystallizes in anhydrous four-sided prisms, terminated by dihedral summits. A solution of the salt gives a black precipitate with subnitrate of mercury, and a white with the per-nitrate of mercury; with nitrate of silver it gives a yellowish white precipitate, which soon becomes black. The trithionate of potash may be decomposed by means of tartaric acid, but the liberated trithionic acid gradually undergoes decomposition into sulphur, and sulphurous and sulphuric acids,  $S_3O_6 = S + SO_2 + SO_3$ . When the trithionates are heated in a closed tube, sulphur

sublimes, sulphurous acid is expelled, and sulphate of the base is left.

(351) TETRATHIONIC ACID, ( $S_4O_6$ ); *Equivalent*, 104.—When hyposulphite of baryta is suspended in water, and iodine is added, iodide of barium is formed, and a new sparingly soluble salt, the tetrathionate of baryta, separates in crystals:



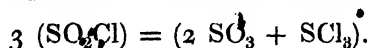
The tetrathionate is purified by recrystallization; and from a solution of this salt pure tetrathionic acid may be prepared by the addition of a quantity of sulphuric acid just sufficient to precipitate the whole of the baryta; the acid may be concentrated *in vacuo* over sulphuric acid. By boiling the solution sulphur is deposited, sulphurous acid escapes, and sulphuric acid remains in the liquid.

(352) PENTATHIONIC ACID, ( $S_5O_6$ ); *Equivalent*, 120.—A solution of sulphurous acid is decomposed by transmitting through it a current of sulphuretted hydrogen; sulphur is deposited, and a new acid remains in solution,  $5 SO_2 + 5 HS = S_5O_6 + 5 S + 5 HO$ . It is very unstable: tetrathionic and trithionic acids form in the solution, attended with a deposition of sulphur. The pentathionate of baryta may be obtained in silky scales by neutralizing the acid with baryta water and precipitating the salt from its aqueous solution by the addition of alcohol. Subnitrate of mercury gives a yellow precipitate in its solution; nitrate of silver a yellow precipitate, which quickly decomposes and becomes black.

The action of sulphuric acid is a valuable means of distinguishing between several of the different classes of the oxy-salts of sulphur. When concentrated sulphuric acid is poured upon the sulphates it evolves no odour, even when heated with them. The sulphites, even in the cold, yield, with dilute sulphuric acid, an odour of sulphurous acid. The hyposulphates emit no odour of sulphurous acid with dilute sulphuric acid in the cold, but evolve sulphurous acid by the aid of heat: whilst dilute sulphuric acid produces with the hyposulphites, in the cold, an odour of sulphurous acid attended with a deposit of sulphur.

(353) CHLOROSULPHURIC ACID, ( $SO_2Cl$ ); *Equivalent*, 67.5.—If equal measures of sulphurous acid and of chlorine, both perfectly dry, be mixed together, no change occurs in diffused daylight, but under the influence of bright sunshine they unite and condense to a colourless liquid, of specific gravity 1.66. It has an extremely pungent odour, and an irritating effect upon the eyes. It boils at

170° F., and emits a vapour of specific gravity 4.665. This substance can scarcely be called an acid, as it does not form any peculiar class of salts. It may be distilled unchanged from caustic lime or baryta; but by admixture with water it is immediately decomposed into sulphuric and hydrochloric acids,  $\text{SO}_2\text{Cl} + \text{HO} = \text{SO}_3 + \text{HCl}$ . An analogous compound may be formed with iodine. These bodies are considered, by H. Rose and by Berzelius, as compounds of sulphuric acid with chloride or iodide of sulphur:



Rose has obtained a fuming oily-looking compound, which boils at 293° F., containing  $\text{SO}_3 + \text{SO}_2\text{Cl}$ , which both Rose and Berzelius regard as  $(5 \text{SO}_3 + \text{SCl}_3)$ . It should be stated, in opposition to this view of Berzelius, that no compound of chlorine,  $\text{SCl}_3$ , is known to exist.

(354) NITROSULPHURIC ACID,  $(\text{SO}_2\text{NO}_2)$ ; *Equivalent*, 62.—Deutoxide of nitrogen and sulphurous acid may be mixed with each other in a dry state without entering into combination, but if a strong solution of potash be thrown up into a jar containing a mixture of 2 volumes of the deutoxide and 1 of sulphurous acid, over mercury, the gas is gradually and completely absorbed. If a solution of ammonia be saturated with sulphurous acid, then mixed with four or five times its bulk of solution of ammonia, and a current of deutoxide of nitrogen be slowly transmitted, whilst the liquid is artificially kept cool, the gas is in great measure absorbed, and beautiful snow-white crystals of nitrosulphate of ammonia,  $\text{NH}_4\text{O}, \text{SO}_2\text{NO}_2$ , are deposited; they may be collected on a filter, washed with a little ice-cold solution of ammonia, and dried *in vacuo* over sulphuric acid.

This salt is a singularly unstable compound; when dissolved in water it begins to undergo decomposition at ordinary temperatures: the presence of a free alkali increases its stability. If an attempt be made to liberate the acid by the addition of another acid to the salt, brisk effervescence, due to the escape of protoxide of nitrogen, takes place, and sulphuric acid remains in the liquid,  $\text{SO}_2\text{NO}_2$  giving  $\text{SO}_3 + \text{NO}$ . Mere admixture of the solution of the nitrosulphate of ammonia with that of many metallic salts, such for instance as sulphate of copper, produces a similar decomposition: probably a double decomposition occurs,  $\text{CuO}, \text{SO}_2 + \text{NH}_4\text{O}, \text{SO}_2\text{NO}_2 = \text{CuO}, \text{SO}_2\text{NO}_2 + \text{NH}_4\text{O}, \text{SO}_3$ ; and the nitrosulphate of copper is immediately resolved into protoxide of nitrogen and sulphate of copper. If the dry nitrosulphate be heated a little



above  $230^{\circ}$ , it is decomposed with explosive evolution of the protoxide of nitrogen.

The nitrosulphates of potash and soda are rather more stable. No insoluble nitrosulphates have been formed; they give no precipitate with baryta water. The nitrosulphates of the alkalis are neutral to test paper, and have a pungent bitterish taste.

(354 bis) *Compounds of Sulphurous and Nitrous Acids—Sulphazotized Acids of Frémy.*—A remarkable series of salts has been described by Frémy (*Ann. de Chimie*, III., xv., 408), formed by the action of sulphurous acid upon nitrite of potash containing a large excess of free alkali. Sulphurous acid combines with the elements of nitrite of potash and water in several different proportions, and forms compounds which crystallize readily, and in which neither sulphurous nor nitrous acid can be detected by the usual tests. The solutions of these salts produce a precipitate in solutions of salts of baryta, which contains the new acid. These compounds are all decomposed by boiling their solutions, and ammonia and sulphuric acid are amongst the products; and some of them even experience a similar decomposition at ordinary temperatures.

The subjoined formulæ will sufficiently indicate the derivation of these salts from nitrite of potash, water, and sulphurous acid:—

Sulphazite of potash,	$3 \text{ KO}, \text{S}_2\text{NH}_3\text{O}_{12}$ or $3 \text{ KO}, \text{NO}_3 + 3 \text{ SO}_2 + 3 \text{ HO}$
Sulphazate of potash,	$3 \text{ KO}, \text{S}_2\text{NH}_3\text{O}_{14}$ or $3 \text{ KO}, \text{NO}_3 + 4 \text{ SO}_2 + 3 \text{ HO}$
Sulphazotate of potash,	$3 \text{ KO}, \text{S}_2\text{NH}_3\text{O}_{16}$ or $3 \text{ KO}, \text{NO}_3 + 5 \text{ SO}_2 + 3 \text{ HO}$
Sulphammonate of potash,	$4 \text{ KO}, \text{S}_2\text{NH}_3\text{O}_{22}$ or $4 \text{ KO}, \text{NO}_3 + 8 \text{ SO}_2 + 3 \text{ HO}$

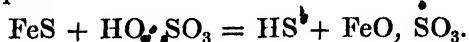
It is remarkable that if nitrite of soda be substituted for nitrite of potash no sulphazotized salts are formed. Indeed, M. Frémy was unsuccessful in his attempts to procure any such compound with soda.

The sulphammonate of potash is easily formed by mixing a solution of sulphite of potash with one of nitrite of potash; the sulphammonate is deposited in beautiful silky needles.

## COMPOUNDS OF SULPHUR WITH HYDROGEN.

(355) **HYDROSULPHURIC ACID:** *Sulphuretted Hydrogen*, (HS); *Equivalent*, 17; *Combining Volume*, 2; *Specific Gravity*, 1.1912.—With hydrogen sulphur forms an important compound, commonly termed sulphuretted hydrogen, but which as it possesses feeble acid properties, may be more fitly termed hydrosulphuric acid. It is formed in small quantities when sulphur is heated in hydrogen gas, but it is always prepared for use by decomposing one of

the metallic sulphides with an acid. For ordinary purposes, about half an ounce of sulphide of iron ( $\text{FeS}$ ), in small fragments, is placed in a bottle and is decomposed in the cold by an ounce of sulphuric acid diluted with six or eight times its bulk of water; gas is immediately formed in abundance: the oxygen of the water enters into combination with the iron, forming oxide of iron, which dissolves in the acid, while the hydrogen takes up the sulphur and escapes.



As the sulphide of iron often contains a portion of metallic iron disseminated through it, the gas is commonly contaminated with free hydrogen. Fig. 265 shows a convenient method of

FIG. 265.

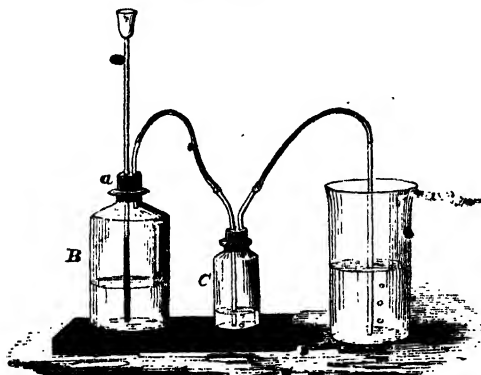
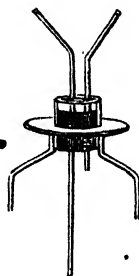


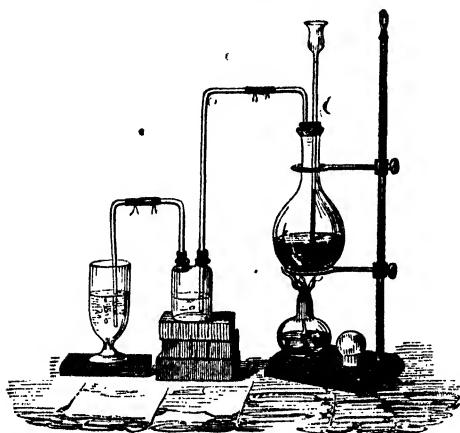
FIG. 266.



mounting an apparatus for disengaging a continuous current of the gas from sulphide of iron. The cork through which the tubes pass is not fitted at once into the bottle, c or d, but is made to fit, as at a, into a piece of stout glass tube, open at both ends, such as is shown in fig. 266; this tube is ground so as to close the neck of the bottle air tight, like an ordinary stopper. The apparatus, which requires to be frequently dismounted in order to be charged afresh, may thus be kept in a serviceable condition without the trouble or loss of time consequent on the frequent renewal of the corks which would be needed unless this expedient were adopted. The various small tubes are connected together by long pieces of vulcanized caoutchouc tubing. When the gas is required in a state of purity, 1 part of powdered sulphide of antimony is substituted for the sulphide of iron: in this case it is necessary to employ 3 or 4 parts of hydrochloric acid of sp. gr. 1.1, and to apply a gentle

heat to the mixture; the apparatus may then be arranged as in fig. 267. In either case the gas requires to be washed before collecting it, in order to remove any particles of the acid or of the

FIG. 267.



metal which may have been carried over with it in mechanical suspension. As the compound of antimony with sulphur is tersulphide ( $\text{SbS}_3$ ) 1 equivalent of it requires 3 equivalents of hydrochloric acid for its decomposition, and furnishes 1 equivalent of terchloride of antimony and 3 equivalents of sulphuretted hydrogen, as may be seen from the subjoined equation.



*Properties.* Hydrosulphuric acid is a transparent colourless gas, of a disgusting odour, resembling that of rotten eggs. It is highly poisonous when respired in a concentrated form, and even when diluted with from 600 to 1200 times its bulk of air, is rapidly fatal to the lower animals. It is inflammable, and burns with a pale bluish flame, depositing sulphur if the supply of air be insufficient for complete combustion. Its density a little exceeds that of atmospheric air, 100 cubic inches weighing rather more than 38 grains.

The proportion of hydrogen in a given volume of the gas may be ascertained by heating some granulated tin in a small retort filled with sulphuretted hydrogen and inverted in a vessel of mercury: the sulphur combines with the tin, whilst the hydrogen which remains occupies when cold the same space as the gas before it was decomposed. Potassium cannot be employed instead of tin in this case, because, though it decomposes the gas, the sulphide of potassium which is formed enters into combination with another portion of the gas without decomposing it.

Sulphurous acid and sulphuretted hydrogen in the presence of moisture, mutually decompose each other, half the oxygen of the sulphurous acid uniting with the hydrogen of the sulphuretted

hydrogen, water and pentathionic acid being formed, whilst sulphur is deposited. For complete decomposition, 2 volumes of sulphuretted hydrogen, and 1 of sulphurous acid, would be requisite.

$$5 \text{ SO}_2 + 5 \text{ HS} = 5 \text{ S} + 5 \text{ HO} + \text{S}_5\text{O}_6.$$

Hydrosulphuric acid is also immediately decomposed by chlorine, bromine, and iodine; sulphur being precipitated, and hydrochloric, hydrobromic, or hydriodic acid being formed by the hydrogen, which combines with one or other of the elements above mentioned.

Under a pressure of about seventeen atmospheres, sulphuretted hydrogen is reducible to a colourless, extremely mobile liquid, which freezes to a transparent mass at a temperature of  $-122^\circ \text{F}$ .

Water dissolves between two and three times its bulk of sulphuretted hydrogen, producing a feebly acid liquid, which has the smell and taste of the gas. When exposed to the air, this solution becomes milky; the hydrogen is slowly oxidized, forming water, and the sulphur separates. If the oxidation of sulphuretted hydrogen take place in a moist atmosphere, a little sulphuric acid is formed, and this action is favoured by the presence of a base to combine with the newly formed acid.

Sulphuretted hydrogen is formed naturally under a variety of circumstances. Whenever a soluble sulphate remains in contact with decaying animal or vegetable matter, the sulphate loses oxygen, which combines with the elements of the decaying substance, whilst sulphide of the metal remains. Sulphate of lime, for example, by the abstraction of 4 equivalents of oxygen, becomes converted into sulphide of calcium. Thus,  $\text{CaO}, \text{SO}_3, - \text{O}_4 = \text{CaS}$ .

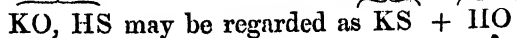
In this way it is formed in many springs, such as those of Harrogate, giving to them their peculiar sulphureous odour; and in a somewhat similar manner, sulphuretted hydrogen forms in large quantities in stagnant sewers and cesspools.

(356) *Hydrosulphates, or Sulphides.* — Hydrosulphuric acid though a feeble acid, combines readily with bases: for example, if the gas be transmitted into a solution of potash or solution of ammonia, it is rapidly absorbed, hydrosulphate of potash,  $\text{KO}, \text{HS}$ , or hydrosulphate of ammonia  $\text{H}_3\text{N}, \text{HS}$ , being formed. Such solutions are, however, generally regarded as sulphides of the metals, because the hydrogen of the acid is exactly equivalent to the oxygen of the base, and is capable, as in the analogous case of the chlorides, of forming water and a metallic sulphide: for example:

Hydrosulphate  
of potash.

Sulphide of  
potassium.

Water.



Moreover, the action of sulphuretted hydrogen in cases in which it occasions a precipitate in the solution of a metallic salt, consists in the formation of an insoluble metallic sulphide—when, for instance, sulphate of copper in solution is treated with sulphuretted hydrogen, an abundant black precipitate of sulphide of copper is produced, water is formed, and the liquid becomes acid from the liberation of sulphuric acid.  $\text{CuO}, \text{SO}_3 + \text{HS}$ , become  $\text{HO}, \text{SO}_3 + \text{CuS}$ .

Sulphuretted hydrogen is in continual requisition in the laboratory as a test for the discovery of metallic bodies: it gives with many metallic salts, characteristic precipitates; for instance, with the compounds of lead it gives a black, with those of arsenic a yellow, and with those of antimony an orange, coloured precipitate. Many metallic solutions, such as those of zinc, iron, and manganese, when acidulated yield no precipitate with it, and it is therefore often employed, in the course of analysis, to separate these metals from others, which are thrown down by it in the form of insoluble sulphides. For this purpose a current of the gas is transmitted through the solution on which it is designed to act. In these cases it is always necessary to purify it from particles held in mechanical suspension, and carried over by the effervescence of the materials employed, ~~and~~ is therefore first allowed to bubble up through a layer ~~of~~ water in a Woulfe's bottle interposed between the generator and the liquid to be submitted to its action.

When the affinity between a metallic oxide and an acid is too great to be overcome by the action of hydrosulphuric acid, the sulphide may notwithstanding be obtained, provided that an alkali be simultaneously presented to the acid of the metallic salt; this may easily be effected by mixing a soluble sulphide with the salt to be decomposed. Thus if sulphate of iron ( $\text{FeO}, \text{SO}_3$ ) be exposed to a current of sulphuretted hydrogen it will experience no change, but if mixed with a solution of sulphide of potassium, a black precipitate of sulphide of iron ( $\text{FeS}$ ) is immediately produced, while sulphate of potash is formed in the solution:  $\text{FeO}, \text{SO}_3 + \text{KS} = \text{KO}, \text{SO}_3 + \text{FeS}$ . The sulphides thus formed are very commonly hydrated compounds: when exposed to the air in their moist condition, many of them absorb oxygen rapidly, some being converted, like sulphide of nickel, into sulphate;  $\text{NiS} + 4\text{O}$  give  $\text{NiO}, \text{SO}_3$ : whilst others are simply converted, like sulphide of iron, into free sulphur and the metallic oxide;  $2\text{FeS} + 3\text{O} = \text{Fe}_2\text{O}_3 + 2\text{S}$ .

Hydrosulphuric acid has a strong disposition to combine with the soluble sulphides. It forms definite compounds with them; thus sulphide of potassium combines with an equivalent of sul-

phuretted hydrogen, forming the compound ( $\text{KS}$ ,  $\text{HS}$ ), and sulphide of ammonium acts in a similar way, producing the ordinary test ( $\text{H}_4\text{NS}$ ,  $\text{HS}$ ) which is used in the laboratory under the incorrect name of hydrosulphate of ammonia. These compounds have a strong odour of sulphuretted hydrogen, and when decomposed by a metallic salt, the hydrosulphuric acid is set at liberty:

Thus,  $\text{H}_4\text{NS}$ ,  $\text{HS} + \text{MnO}$ ,  $\text{SO}_3 = \text{H}_4\text{NO}$ ,  $\text{SO}_3 + \text{MnS} + \text{HS}$ .

Many of the hydrosulphates and sulphides are easily detected by the smell of sulphuretted hydrogen which they evolve when moistened with hydrochloric acid. A very minute trace of the gas may be detected by placing a piece of paper moistened with acetate of lead in the upper part of the tube or vessel in which the suspected sulphide has been mixed with acid, and closing the vessel; after the lapse of a few minutes, a brown or black tinge occurs, owing to the formation of sulphide of lead, if sulphuretted hydrogen be evolved. When heated before the blowpipe, the sulphides emit the odour of sulphurous acid.

(357) PERSULPHIDE OF HYDROGEN, ( $\text{HS}_2$ ?) — In order to procure this compound it is usual to prepare first a persulphide of calcium ( $\text{CaS}_2$ ), which may be formed by boiling equal weights of slacked lime and powdered sulphur in water; the persulphide of calcium dissolves mixed with a corresponding amount of hyposulphite of lime,  $3 \text{ CaO} + 12 \text{ S} = \text{CaO}$ ,  $\text{S}_2\text{O}_2 + 2 \text{ CaS}_2$ : the undissolved sulphur is separated by filtration. On allowing the deep yellow liquid to fall into hydrochloric acid diluted with 2 parts of water, and gently warmed, persulphide of hydrogen separates as an oily liquid of sp. gr. 1.769, having a smell and taste resembling hydrosulphuric acid: it burns with a blue flame. In many of its properties it presents a striking analogy with deutoxide of hydrogen; it possesses bleaching powers, is very prone to spontaneous decomposition into sulphur and sulphuretted hydrogen, it is rendered more stable by the presence of acids, and is immediately decomposed by alkalis. The latter circumstance renders it necessary in preparing this compound always to add the sulphide of calcium to the acid—not the acid to the sulphide, which would be attended with an escape of hydrosulphuric acid and a precipitation of finely divided sulphur. The sulphur which is precipitated in this manner from an alkaline persulphide, was formerly employed in medicine under the term of *lac sulphuris*.

Oxides of manganese and of silver decompose persulphide of hydrogen by mere contact with the liquid, producing a violent

effervescence, attended with disengagement of sulphuretted hydrogen. Persulphide of hydrogen dissolves sulphur freely, and hence its exact composition is not certainly known, since a portion of sulphur derived from the hyposulphite of lime formed in preparing the sulphide of calcium, always precipitates along with the persulphide, and dissolves in the liquid obtained.

(358) BISULPHIDE OF CARBON: *Sulphocarbonic Acid*, ( $\text{CS}_2$ ), *Equivalent*, 38.—Only one compound of sulphur with carbon has as yet been obtained. It may be prepared by heating fragments of charcoal to bright redness in an earthen retort, furnished with a tubulure into which is luted a porcelain tube, which passes nearly to the bottom of the retort: the tube is provided at its upper extremity with a sound cork. From time to time this cork is withdrawn, and a fragment of sulphur is dropped into the retort; the cork is then immediately replaced, the sulphur melts, and is converted into vapour; at this elevated temperature the carbon combines with it, and the bisulphide thus obtained may be condensed in vessels cooled by ice. It is yellow when first formed, and contains an excess of sulphur; but by redistillation it may be obtained in a state of purity. It is a colourless liquid of high refracting power, of an acid, pungent taste, and a foetid, peculiar, sulphurous odour. It is heavier than water, in which it is insoluble, having a specific gravity of 1.272 at  $60^\circ \text{F}$ . In ether and alcohol it is freely soluble. It is exceedingly volatile, boils at  $118^\circ.5$ , and emits a vapour of a density of 2.6447 (Gay Lussac), of which the combining volume is 2 : 2 equivalents of sulphur, and 1 equivalent of carbon vapour being condensed into the space occupied by 2 equivalents of oxygen. Bisulphide of carbon has never hitherto been frozen; hence it has been employed sometimes in the construction of thermometers destined to measure very intense degrees of cold.

Bisulphide of carbon is highly inflammable, and burns with a blue flame producing sulphurous and carbonic acid gases. It dissolves sulphur freely, and, by spontaneous evaporation, leaves it in rhombic octohedra. Phosphorus is also freely dissolved by it, and may be obtained in crystals by slow evaporation. Iodine, bromine, and chlorine are likewise readily dissolved by the bisulphide of carbon. Berzelius considers bisulphide of carbon as a sulphur-acid: it corresponds to carbonic acid, and contains 2 equivalents of sulphur in the place of 2 equivalents of oxygen: it combines with the sulphides of the alkali metals, forming a species of salts which are called sulphocarbonates.

• (359) DICHLORIDE OF SULPHUR, ( $\text{S}_2\text{Cl}$ ); *Equivalent*, 67.5.—Chlorine and sulphur form two compounds with each other; they

combine gradually at common temperatures, but if heated together the union is rapid. In preparing the dichloride of sulphur, a current of dry chlorine is usually directed towards the bottom of a retort containing melted sulphur; the resulting chloride must be collected in a perfectly dry receiver, kept cool: it may be purified from excess of chlorine by redistillation from flowers of sulphur: a yellow volatile liquid, of penetrating, peculiar, and disagreeable odour, is thus formed. It emits fumes on exposure to the air, owing to its action on the atmospheric moisture. When dropped into water, it falls to the bottom, and is slowly decomposed into hydrochloric and sulphurous acids and free sulphur. It has a specific gravity of 1.628, and boils at  $280^{\circ}$  F., emitting a vapour of specific gravity 4.70 (Dumas). It acts powerfully on mercury when brought into contact with it, and dissolves sulphur freely.

A CHLORIDE OF SULPHUR ( $\text{SCI}$ ), *Equivalent*, 51.5, may be formed by saturating the preceding compound with chlorine; it is a deep red liquid, of specific gravity 1.625; it fumes strongly in the air, and is decomposed into dichloride of sulphur and free chlorine in the direct rays of the sun. It is partially decomposed by boiling it.

The *bromides* of sulphur are liquids analogous to the chlorides. The *iodide* is a crystalline, brittle, steel-grey solid.

(360) BISULPHIDE OF NITROGEN ( $\text{S}_2\text{N}$ ), *Equivalent*, 46; (Fordos and Gélis, *Ann. de Chimie*, III., xxxii. 389). This compound is obtained when chloride of sulphur is dissolved in ten or twelve times its bulk of bisulphide of carbon, and decomposed by a current of dry ammoniacal gas. The gas is transmitted till the brown colour of the precipitate which is formed, disappears; the yellow liquid is filtered from the muriate of ammonia, and left to spontaneous evaporation; beautiful golden yellow rhombic crystals of sulphide of nitrogen speedily form. The reaction which attends its formation is very complicated, and has not been completely ascertained. Sulphide of nitrogen detonates powerfully by percussion, and explodes when heated to  $314^{\circ}$  F. It has a faint smell, adheres strongly to paper if rubbed on it, and irritates the mucous membrane of the eyes and nose most painfully. Bisulphide of carbon dissolves it pretty readily; alcohol, ether, and oil of turpentine, very sparingly; water does not dissolve it, but slowly decomposes the compound.

Sulphur occurs also in a few compounds of organic origin: it enters into the composition of many foetid volatile oils, and forms a necessary ingredient in the muscular tissue, and several other important structures of the animal economy.



## § II. SELENIUM.

*Symbol, Se ; Equivalent, 39.62 ; Specific Gravity in the Solid State, 4.8.*

(361) *Selenium* is a rare elementary body, discovered by Berzelius in the refuse of a sulphuric acid manufactory, near Fahlun. It derives its chief interest from the remarkable analogy to sulphur which it presents. Selenium always occurs in combination, but it is found only in small quantities, and usually in the form of selenide of iron, of copper, or of silver.

The Fahlun selenium residue is mixed with nitrate and carbonate of potash, and deflagrated; that is to say, it is thrown in small quantities at a time into a red-hot crucible, in which it burns vividly. The selenium and other bodies with which it is associated are oxidized at the expense of the oxygen of the nitre. Selenic acid is formed, and by uniting with the disengaged potash of the nitre, a seleniate of potash is produced. The mass is digested in water, acidulated with hydrochloric acid, and evaporated down to a small bulk. The selenic acid is thus reduced to selenious acid (363), and the selenious acid, when treated with a current of sulphurous acid, yields a precipitate of reduced selenium as a red, flocculent, amorphous powder (362).

When collected and dried, the pulverulent selenium begins to soften at a temperature below that of boiling water; and at a few degrees above  $212^{\circ}$ , it melts; on cooling, it forms a brittle solid, with glassy fracture, metallic lustre, and deep-brown colour: in specific gravity it varies from 4.3 to 4.8. It has neither taste nor smell; it is insoluble in water, and is a non-conductor of heat and electricity. When melted it is ductile, and may be drawn out into fine threads; but it is not easily obtained in crystals. Selenium may however be obtained both in an amorphous and a crystalline condition. According to Hittorf (*Pogg. Ann.* lxxxiv., 214), the fusing point of the crystalline variety is  $420^{\circ}$  F., and in passing from the amorphous to the crystalline form, a considerable evolution of heat occurs. When heated in the air, it does not readily take fire; it burns with a blue flame, but part volatilizes in red fumes, emitting an odour resembling that of bisulphide of carbon. This is due to the formation of a protoxide of selenium, which however is not acid. If heated in close vessels, selenium boils below redness, and gives off a deep yellow vapour, which condenses in red flowers, or opaque metallic-looking drops. Oxygen forms with

selenium two acids ; the first corresponding with sulphurous, and the second with sulphuric acid.

(362) SELENIOS ACID, ( $\text{SeO}_2$ ), *Equivalent*, 55.6, may be obtained by burning selenium in a current of oxygen, but it is usually prepared by boiling selenium with nitric acid or with aqua regia. The selenium is gradually oxidized, and dissolves ; the excess of nitric acid may be expelled by heat, leaving the selenious acid as a white mass, which does not melt on further urging the heat, but sublimes below redness, forming a yellow vapour, and condensing again in beautiful snow-white, prismatic, anhydrous needles. The crystals are deliquescent, and in solution form a strong acid liquid, with a sour burning taste. Selenious acid is speedily deoxidized by iron or by zinc, which, when digested in the acid, occasions the deposition of the selenium in the form of a reddish-brown powder.

*Selenites*.—Most of the selenites, except those of the alkalis, are insoluble in water, but soluble in nitric acid. With the alkalis three classes of salts are formed : neutral selenites, which contain 1 equivalent of acid to 1 of base ; biselenites, with 2 equivalents of acid to 1 of base ; and quadriselenites, with 4 equivalents of acid to 1 of base. The selenites are easily recognised when heated on charcoal before the blowpipe in the reducing flame, by the peculiar odour of selenium which they emit ; the selenites in solution, when treated with sulphurous acid, give a reddish-brown precipitate of reduced selenium ;  $\text{SeO}_2 + 2 \text{SO}_2 = \text{Se} + 2 \text{SO}_3$ .

(363) SELENIC ACID, ( $\text{SeO}_3$ ), *Equivalent*, 63.6, is best obtained by deflagrating selenium or any selenite with nitre. The residue is dissolved in water, and mixed with solution of nitrate of lead ; an insoluble seleniate of lead precipitates, which, if suspended in water, may be decomposed by a current of sulphuretted hydrogen. Sulphide of lead is thus formed, and selenic acid is set at liberty :  $\text{PbO}, \text{SeO}_3 + \text{HS} = \text{PbS} + \text{H}_2\text{O}, \text{SeO}_3$ . The acid may be separated by filtration, and concentrated by evaporation till it has a specific gravity of 2.6 ; if heated beyond  $550^\circ$  it is decomposed into selenious acid and oxygen. Sulphurous acid is without effect upon selenic acid, but hydrochloric acid decomposes it when heated with it, chlorine and selenious acid being liberated. In its properties it closely resembles sulphuric acid, and its salts are isomorphous with the sulphates of the same bases.

*Seleniates*.—Solutions of the seleniates give white precipitates with salts of baryta, strontia, and lead, owing to the formation of insoluble seleniates of these bases. These precipitates are insoluble in dilute nitric acid. When the soluble seleniates are boiled with

hydrochloric acid, selenic acid, is liberated, and is reduced to the form of selenious acid;  $\text{SeO}_3 + \text{HCl} = \text{SeO}_2 + \text{HO} + \text{Cl}$ : sulphurous acid will then precipitate reduced selenium from the solution. On charcoal before the blowpipe in the reducing-flame, the seleniates emit the characteristic odour of selenium.

(364) SELENIURETTED HYDROGEN—*Hydroselenic Acid*, ( $\text{HSe}$ ); *Equivalent*, 40.6; *Specific Gravity*, 2.795 (Bineau).—This substance is a colourless gas, which resembles hydrosulphuric acid, but its odour is more offensive. Berzelius found that the inhalation of a bubble of the gas no larger than a pea deprived him of the sense of smell for several hours. It is soluble in water, and precipitates many metals from their salts in the form of selenides. Its solution, if exposed to the air, absorbs oxygen and deposits selenium. Seleniuretted hydrogen is obtained by acting on selenide of potassium or of iron, with dilute hydrochloric or sulphuric acid.

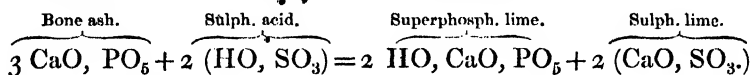
### § III. PHOSPHORUS.

*Symbol*, P; *Equivalent*, 32; *Combining Volume of Vapour*, 1; *Specific Gravity of Vapour*, 4.355.

(365) Phosphorus is never met with in nature in the uncombined state, but it occurs in small quantity as phosphate of lime, as a constituent of the primitive and volcanic rocks, by the gradual decay of which it passes into the soil; from the soil it is extracted by plants, which accumulate it, particularly in their seeds, in quantity sufficient for the support of the various tribes of animals which they supply with food. In the animal system it is collected in large quantity, and, when combined with oxygen and lime, as phosphate of lime, it forms the principal earthy constituent of the bones of the vertebrata. Phosphorus also appears to be essential to the exercise of the higher functions of the animal, since it exists as a never-failing ingredient in the substance of which the brain and nerves are composed.

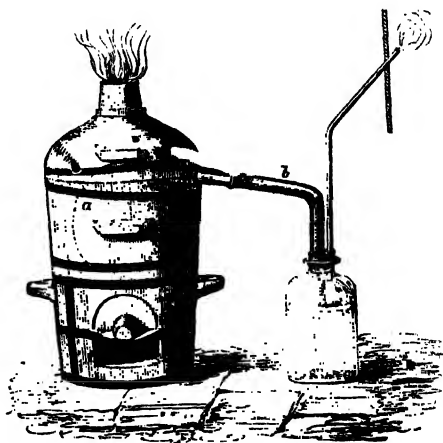
*Preparation*.—Phosphorus was originally extracted from the salts contained in urine, but it is now obtained almost exclusively from the bones of animals. In order to prepare it, bones are burned to whiteness by calcining them in an open fire for some hours; they are then reduced to powder; 3 parts of this bone-ash are mixed with 2 of concentrated sulphuric acid, and 18 or 20 parts of water. The mixture is allowed to stand for two or three days, after which it is placed upon a strong linen filter, and the acid liquid is sepa-

rated from the sulphate of lime by pressure; the residue is further washed with water, and the washings are added to the filtered solution. In this process the sulphuric acid is added in such quantity as partially to decompose the phosphate of lime; two-thirds of the lime are removed by it in the form of an insoluble sulphate of lime, the remaining third being left in combination with the whole of the phosphoric acid, with which it forms a compound readily soluble in water, frequently described as *superphosphate of lime* ( $\text{CaO}, \text{PO}_5$ ). The reaction may be thus expressed in symbols:—



This acid solution is evaporated to a syrup, then mixed with one-fourth of its weight of charcoal, and heated to incipient redness in an iron pot, stirring constantly. The mass, when dry, is transferred to an earthen retort, *a*, fig. 268, which is covered externally with a thin paste, consisting of a mixture of equal parts of borax and fire clay, to render the retort less porous. It is then exposed to a heat which is slowly raised to a full red. Phosphorus gradually rises in vapour, and is conveyed by means of a wide copper tube, bent as at *b*, so as to dip into water contained in a vessel which is provided with a smaller tube, open at both ends, for conveying the uncondensed gases into a chimney. The phosphorus condenses in yellow drops. It is found necessary to convert the phosphate into superphosphate of lime, since the bone-ash, when heated with charcoal, does not part with its phosphorus. The superphosphate of lime in contact with charcoal is decomposed; the lime retains sufficient phosphoric acid to reconstitute bone earth, which remains unchanged in the retort, while the excess of acid and the water which the mass always retains are decomposed by the charcoal; hydrogen, carbonic oxide, and phosphorus, are the results. Gaseous matters escape, therefore, during the whole opera-

Fig. 268.



tion:  $3(2 \text{ HO, CaO, PO}_5) = 3 \text{ CaO, PO}_5 + 6 \text{ HO} + 2 \text{ PO}_5$ ; and  $2 \text{ PO}_5 + 6 \text{ HO} + 16 \text{ C} = 2 \text{ P} + 6 \text{ H} + 16 \text{ CO}$ .

To render the phosphorus perfectly pure, it is fused under warm water, squeezed through wash leather; again melted, first under ammonia, and then under a solution of bichromate of potash in dilute sulphuric acid. The easy fusibility of phosphorus enables it to be moulded into sticks with facility; it is melted under water and forced into tubes, in which it is allowed to solidify.

*Properties.*—Phosphorus is a soft, semi-transparent, colourless, waxy-looking solid, which fumes in the air, emitting white vapours of an alliaceous odour; when taken internally it acts as an irritant poison. It has a specific gravity of 1.83 at 50° F. (Schrötter). It fuses at 111° 5', and if melted under an alkaline liquid and allowed to cool undisturbed, it will long continue fluid at ordinary temperatures, but when touched with a wire or a glass rod it solidifies suddenly. It is exceedingly inflammable, taking fire in the open air at a temperature very little above its fusing point. If it contain impurities, such as oxide of phosphorus, it takes fire still more easily. Great caution is therefore required in handling it; it is better always to cut it under water. The burns occasioned by melted phosphorus are deep and often extremely severe, from the difficulty of extinguishing the flame.

Phosphorus burns with a brilliant white flame, and emits dense white fumes of phosphoric acid. In close vessels it boils at about 550°, giving off a colourless gas, of which 100 cubic inches weigh about 135 grains. Phosphorus is insoluble in water; it is slightly soluble in ether, but more so in naphtha. It is freely dissolved by didiodide of sulphur, and by the bisulphide of carbon; by allowing its solution in either liquid to evaporate slowly in a current of hydrogen or carbonic acid, the phosphorus may be obtained crystallized in rhombic dodecahedra.

Phosphorus is always preserved under water, as when exposed to the air, it at all temperatures above 32° gradually combines with oxygen, and undergoes a slow combustion; under these circumstances in a darkened room it emits a pale greenish light, (hence its name, 'light-bearer,') attended with the production of the white fumes and the garlic odour already mentioned. The luminosity of phosphorus is prevented by the admixture of certain inflammable vapours and gases in minute quantity with the atmosphere; if air be mixed with either  $\frac{1}{100}$ th of its bulk of olefiant gas,  $\frac{1}{150}$ th of naphtha, or  $\frac{1}{44}$ th of oil of turpentine, a stick of phosphorus no longer appears luminous when exposed to its action (Graham).

It is remarkable that in pure oxygen the luminosity is not observed until the temperature rises to  $60^{\circ}$ , unless the gas be rarefied, or be diluted with some other gas.

Berzelius states that phosphorus may become luminous at ordinary temperatures without undergoing oxidation, but simply from its volatilization, and that the emission of light occurs in hydrogen, nitrogen, and even in the vacuum of the barometer; but Schrötter has shown, by careful and conclusive experiments, that in all cases where light appears to be emitted during this volatilization, it is due to the presence of traces of oxygen (*Chem. Gaz.* xi. 312.)

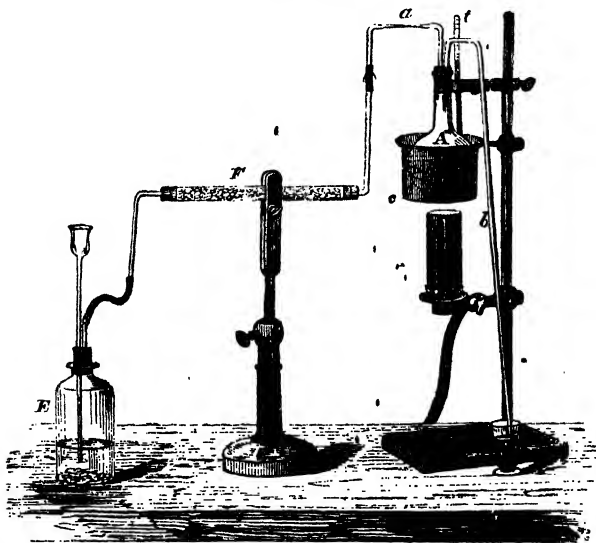
(366) *Different forms of Phosphorus.*—Phosphorus assumes several different forms under the influence of causes apparently trifling. The transparent variety has been already mentioned; this, when kept exposed to light under water, forms a second variety, which is white and opaque, and somewhat less fusible. A third form is obtained by suddenly cooling melted phosphorus; it is perfectly black and opaque; whilst a fourth modification, analogous to viscous sulphur, may be obtained by heating very pure phosphorus to near its boiling point and suddenly cooling it. A fifth form occurs in the shape of red scales, which are obtained by the spontaneous sublimation of phosphorus in the Torricellian vacuum when exposed to the rays of the sun.

This red amorphous form of phosphorus has been carefully studied by Schrötter (*Ann. de Chimie*, III. xxiv. 406); in many of its properties it differs remarkably from the waxy-looking stick phosphorus. It may be exposed to the air without undergoing alteration or emitting any odour. It is not soluble in either bisulphide of carbon, trichloride of phosphorus, or naphtha. The density of amorphous phosphorus exceeds that of the vitreous form, the red powder, according to Brodie, having a specific gravity of 2.14. It may be heated in the open air without change till the temperature reaches  $500^{\circ}$  F.; at this point it melts and bursts into flame, and burns with the dazzling brilliancy of common phosphorus, emitting dense fumes of phosphoric acid. If the operation be performed in a tube from which air is excluded, the red powder is found to be reconverted into ordinary phosphorus. Chlorine acts directly upon red phosphorus without the application of heat: the temperature rises, but the phosphorus does not take fire. When rubbed with chlorate of potash it detonates, very slight friction being sufficient to produce the action: peroxide of manganese and peroxide of lead act in a similar way, but less readily. Schrötter has attempted, though as yet with imperfect success, to apply this form of

phosphorus to the preparation of lucifer matches. Immense quantities of phosphorus are consumed in this manufacture. In the usual mode of preparing these matches, the ends of the pieces of wood are first gummed and dusted over with sulphur, and then tipped with a mixture, in which the chief ingredients are, an emulsion of phosphorus in glue, and chlorate of potash, or oxide of manganese. The manufacture is one attended with danger, from the highly inflammable and explosive nature of the ingredients used; but in addition to this risk, those employed in the business are liable to a distressing form of caries of the lower jaw, arising from the action of the fumes of phosphorus upon those who inhale them. Of these evils, the first would be greatly lessened, and the second altogether avoided by the use of the amorphous phosphorus of M. Schrötter.

This variety of phosphorus may be obtained by placing a quantity of dried common phosphorus in the bulb of a flask, *A*, fig. 269, to the neck of which a long narrow tube, *b*, bent down-

FIG. 269.



ward, is attached; the open end of this tube dips into a little mercury; the air in the flask is displaced by means of a current of carbonic acid, which is supplied from the bottle, *E*, and dried by passing through the tube, *e*, filled with chloride of calcium; the tube is then sealed at the narrow portion, *a*, and the apparatus which supplied the carbonic acid is removed. Heat is next applied to the flask by means of an oil bath, *c*: the phosphorus melts readily, but by regulating the heat steadily between  $450^{\circ}$

and  $460^{\circ}$ , by means of the thermometer, *t*, and maintaining it for thirty or forty hours, almost all the phosphorus will become converted into the solid amorphous variety. When the change appears to be complete, the apparatus is allowed to cool; bisulphide of carbon is then poured upon the mass in the flask, and digested on it for some hours; this is poured off, and fresh bisulphide added, the digestion being repeated as long as any phosphorus dissolves; this may be known by allowing a few drops of the decanted liquid to evaporate spontaneously in a watch glass; any dissolved phosphorus will be left behind.

The red powder thus obtained, if not quite free from unaltered phosphorus, takes fire spontaneously; but if quite pure, it suffers no change by exposure to the air. The higher the temperature at which the transformation is effected the deeper is the colour, which in the finest specimens rivals that of vermilion. By heating the phosphorus more strongly during its preparation, the change may be produced much more rapidly, but the phosphorus then assumes the form of coherent flakes, which are more difficult to purify and to detach from the vessel in which they are prepared. This form of phosphorus has been manufactured at Birmingham, by Messrs. Sturge, on a considerable scale. The process, however, requires much care, and is not unattended with danger, as if the red powder be heated up to the point at which its re-conversion into the transparent variety takes place, the whole mass suddenly passes back into the ordinary form, with a copious evolution of heat, followed by the sudden formation of a large volume of the vapour of phosphorus. The amorphous phosphorus, therefore, appears to contain a large amount of heat in the latent condition, which is liberated as it passes back into the vitreous state. The changes produced by heat in phosphorus may be readily watched by placing a few fragments of well dried phosphorus in a tube, upon which two or three bulbs have been blown, then expelling the air by a current of carbonic acid, and sealing one end of the tube; the open end being made to dip into mercury. On applying heat to the phosphorus it becomes red, but on continuing to raise the temperature it distils over in perfectly colourless transparent drops, which frequently remain liquid for some hours, though they ultimately solidify to a transparent, colourless mass.

Owing to its strong affinity for oxygen, phosphorus reduces some of the oxidized compounds of the metals to the metallic state: a stick of phosphorus placed in a solution of chloride of gold or of nitrate of silver becomes speedily incased in reduced gold or silver.

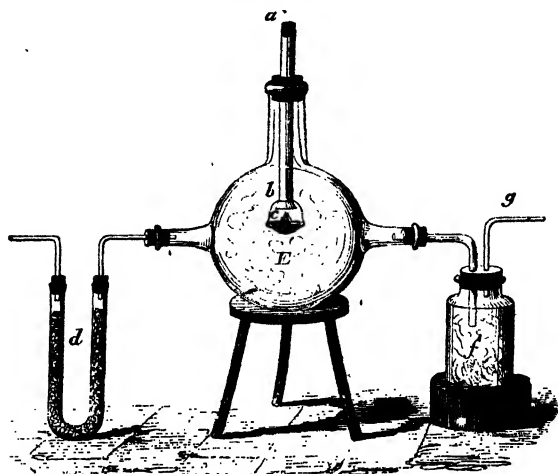


(367) Phosphorus forms four well defined compounds with oxygen. Three of these possess an acid character:—

Phosphoric acid . . . . .	$\text{PO}_5$ .
Phosphorous acid . . . . .	$\text{PO}_3$ .
Hypophosphorous acid . . . . .	$\text{PO}$ .
Oxide of phosphorus . . . . .	$\text{P}_2\text{O}$ .

(368) PHOSPHORIC ACID, ( $\text{PO}_5$ ); *Equivalent*, 72. — The most important of the oxides of phosphorus is phosphoric acid, which is the sole product of the rapid combustion of phosphorus in

FIG. 270.



oxygen or atmospheric air. By means of the apparatus shown in fig. 270, a large quantity of phosphoric acid may be readily obtained in a few hours: it is a three-necked globe, in the centre of which is suspended a porcelain dish, *c*; this dish is attached by platinum wire to the wide tube,

*a b*, which is closed at top with a sound cork; the bottle, *f*, is connected by the tube, *g*, with an aspirator, or other convenient means of maintaining a continuous current of air through the apparatus: the air as it enters is thoroughly dried by passing over pumice moistened with sulphuric acid, in the tube, *d*. A fragment of well dried phosphorus is placed in the dish *c*, and kindled by touching it with a hot wire. As the phosphorus burns away fresh pieces are added through the aperture *a*, which is again immediately closed with the cork. Phosphoric acid is thus obtained as a snow-white, flocculent, uncrystalline, anhydrous, but extremely deliquescent, powder. When dropped into water it combines with it, emitting a hissing noise; the greater part instantly dissolves, leaving a few gelatinous flocculi, which slowly disappear. After it has once been dissolved it cannot again be completely deprived of water, unless it be made to enter into combination with a base, such as soda or oxide of lead.

The base in this case unites with the acid and displaces the water.

(369) *Hydrates of Phosphoric Acid.*—In a hydrated state the acid is generally procured by boiling phosphorus in nitric acid diluted till of a specific gravity of 1.20. The phosphorus becomes oxidized by the nitric acid, which is decomposed with escape of deutoxide of nitrogen, and the phosphoric acid dissolves as it is formed. When the phosphorus has all disappeared, the excess of nitric acid is expelled by evaporating the liquid in a platinum vessel until dense white fumes begin to arise: on cooling, the acid solidifies to a transparent glassy mass, frequently termed glacial phosphoric acid. The glacial acid is extremely deliquescent, producing a solution which, when saturated, has a sp. gr. of 2.0. It is intensely acid but not caustic.

The oxidation of phosphorus by nitric acid furnishes an easy means of ascertaining the composition of phosphoric acid. For this purpose, 32 grains of phosphorus are boiled in a glass retort with pure dilute nitric acid. The greater part of the excess of water and nitric acid having been distilled off, the acid solution is added to 350 grains of oxide of lead, in a weighed platinum dish: the liquid is slowly evaporated and the residue ignited; by a red heat the whole of the nitric acid is expelled, and the phosphoric acid alone remains in combination with the lead. The oxide and acid together will be found to weigh 422 grains, showing an increase in weight upon the phosphorus and oxide of lead of 40 grains: 32 parts of phosphorus therefore require 40 parts of oxygen for conversion into phosphoric acid.

A less pure acid is procured by adding to a solution of superphosphate of lime (prepared from bones by the process already described as a preliminary step towards procuring phosphorus) carbonate of ammonia till effervescence ceases; tribasic phosphate of lime is precipitated, leaving phosphate of ammonia in solution. The precipitated phosphate of lime is separated by filtration, the liquid evaporated to dryness, and the residue ignited. Ammonia is expelled, and phosphoric acid (contaminated with all the soluble salts which the bones contained) remains behind.

Hydrated phosphoric acid cannot be completely deprived of water by ignition; for when heated to redness, the acid sublimes with the water. There are three different hydrates of phosphoric acid, each of which possesses the properties of a distinct acid: viz.

the protohydrate of phosphoric acid . . .  $\text{HO}, \text{PO}_5$ ,  
 the deutohydrate of phosphoric acid . . .  $2 \text{HO}, \text{PO}_5$ ,  
 the tritohydrate of phosphoric acid . . .  $3 \text{HO}, \text{PO}_5$ .

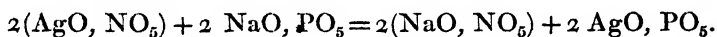
These different hydrates of the acid retain their peculiar characteristics when dissolved in water, and combine with 1, with 2, or with 3 equivalents of bases to form salts, according as the protohydrate, the deutohydrate, or the tritohydrate is employed. Owing to the important influence which the study of these compounds has exercised upon the theory of saline combinations in general, it will be necessary to examine them somewhat in detail.

(370) *Tritohydrate* ( $3 \text{ HO}, \text{PO}_5$ ).—If the liquid formed by dissolving the glacial acid in water be boiled for some time, and carbonate of soda be then added until the solution becomes slightly alkaline, a tribasic phosphate of soda and water ( $2 \text{ NaO}, \text{HO}, \text{PO}_5 + 24 \text{ aq}$ ) is obtained, which on evaporation crystallizes in large transparent rhombic prisms. If this solution be mixed with nitrate of silver, also in solution, a canary-yellow precipitate of tribasic phosphate of silver,  $3 \text{ AgO}, \text{PO}_5$  is formed. Although this solution was neutral or slightly alkaline before admixture with nitrate of silver, it will be found afterwards to have a decided acid reaction, nitric acid being liberated;  $2 \text{ NaO}, \text{HO}, \text{PO}_5 + 3 (\text{AgO}, \text{NO}_5) = 2 (\text{NaO}, \text{NO}_5) + \text{HO}, \text{NO}_5 + 3 \text{ AgO}, \text{PO}_5$ . Acetate of lead may be used as a precipitant instead of nitrate of silver, and in this case a white triphosphate of lead;  $3 \text{ PbO}, \text{PO}_5$  subsides. If this phosphate of lead be well washed, suspended in water, and exposed to the action of a current of sulphuretted hydrogen, pure tritohydrate of phosphoric acid is liberated and dissolves in the liquid, whilst the black insoluble sulphide of lead is formed;  $3 \text{ PbO}, \text{PO}_5 + 3 \text{ HS} = 3 \text{ HO}, \text{PO}_5 + 3 \text{ PbS}$ . By filtration, the sulphide of lead is removed, and the acid may be obtained, by evaporation in vacuo over sulphuric acid, in deliquescent crystalline plates. It requires 3 equivalents of a base for saturation. The salts of this hydrate form the common tribasic phosphates.

The soluble salts of this variety of phosphoric acid are characterized by the yellow phosphate of silver which their neutral solutions form with nitrate of silver, and by the crystalline precipitate which they yield when a clear solution of sulphate of magnesia, rendered alkaline by ammonia, is briskly stirred with them; this precipitate is insoluble in water which contains free ammonia, it consists of ( $2 \text{ MgO}, \text{NH}_4\text{O}, \text{PO}_5 + 12 \text{ HO}$ ); when ignited, it becomes converted into ( $2 \text{ MgO}, \text{PO}_5$ ), and is frequently employed as a means of estimating the amount of phosphates in solutions which contain them. Neutral solutions of the phosphates give precipitates with salts of baryta and lime; the phosphates of baryta and lime dissolve readily in acetic acid. The quantity of phosphoric acid in

a solution may also be ascertained, if neither sulphuric nor hydrochloric acid be present, by means of acetate of lead; the solution, before this salt is added to it, should be neutralized by ammonia, and then acidulated freely with acetic acid; the precipitate, ( $2 \text{ PbO}$ ,  $\text{HO}$ ,  $\text{PO}_5$ ), should be well washed and ignited, after which it becomes anhydrous. With sesquioxide of iron phosphoric acid forms an insoluble buff-coloured precipitate, ( $\text{Fe}_2\text{O}_3$ ,  $\text{PO}_5$ ), which is also sometimes employed to estimate the quantity of phosphoric acid in a solution.

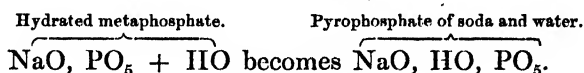
(371) *Deutohydrate, or Pyrophosphoric Acid*, ( $2 \text{ HO}$ ,  $\text{PO}_5$ ).—When rhombic phosphate of soda,  $2 \text{ NaO}$ ,  $\text{HO}$ ,  $\text{PO}_5 + 24 \text{ aq}$ , is exposed to heat, it melts in its water of crystallization; and by continuing to apply to it a temperature not exceeding  $300^\circ \text{ F}$ ., it may be reduced to a hard, white, saline mass, which may be redissolved in water with all its former properties. The dry mass consists of  $2 \text{ NaO}$ ,  $\text{HO}$ ,  $\text{PO}_5$ . If however it be heated to redness before redissolving, 1 equivalent of water is expelled: the residue is found to consist of  $2 \text{ NaO}$ ,  $\text{PO}_5$ , and the phosphoric acid is reduced to the dibasic variety; for on redissolving it in water and evaporating the solution, the liquid no longer yields rhombic crystals, but furnishes acicular crystals, composed of  $2 \text{ NaO}$ ,  $\text{PO}_5$ ,  $10 \text{ aq}$ ; and the solution, instead of yielding a yellow precipitate with nitrate of silver, now gives a white one, consisting of  $2 \text{ AgO}$ ,  $\text{PO}_5$ . In this case the solution, if neutral before intermixture with the silver salt, remains neutral afterwards, as no free acid is liberated:—



With solution of acetate of lead this salt also occasions a white precipitate, the composition of which is represented by the formula  $2 \text{ PbO}$ ,  $\text{PO}_5$ ; and if the lead salt be decomposed with sulphuretted hydrogen, it yields the deutohydrate of phosphoric acid,  $2 \text{ HO}$ ,  $\text{PO}_5$ . The excess of sulphuretted hydrogen must be got rid of by exposure to the air, (not by heat, otherwise the tribasic hydrate is formed,) and the acid may be obtained in crystals by evaporation in vacuo over sulphuric acid. The dibasic phosphate of soda, from the mode in which it is obtained, is often termed the *pyrophosphate* of soda, and the corresponding dibasic salts of the acid, *pyrophosphates*. No solid pyrophosphate of potash or of ammonia can be obtained; these salts are stable while in solution, but on evaporation they become converted into tribasic phosphates by the assimilation of water. (Graham.)

(372) *Protohydrate, or Metaphosphoric Acid*, ( $\text{HO}$ ,  $\text{PO}_5$ ).—If in preparing the rhombic phosphate of soda, (370) two equal portions

of phosphoric acid be taken, and after neutralizing one portion with carbonate of soda, as above directed, the second quantity of acid be added to the neutralized solution, a tribasic phosphate of soda, consisting of  $\text{NaO}$ ,  $2 \text{HO}$ ,  $\text{PO}_5$ , will be obtained on evaporating the liquid to dryness; but on igniting the residue, the 2 equivalents of water will be expelled, and a fusible monobasic phosphate, or *metaphosphate*, of soda,  $\text{NaO}$ ,  $\text{PO}_5$ , will remain, in the form of a transparent glass. This, if dissolved in water, gives with nitrate of silver a gelatinous white precipitate, different in appearance and composition from either of the former phosphates of silver; it contains  $\text{AgO}$ ,  $\text{PO}_5$ , and is soluble in excess of the soda salt. With acetate of lead a white precipitate also is formed,  $\text{PbO}$ ,  $\text{PO}_5$ ; it is fusible in boiling water, and when decomposed with sulphuretted hydrogen, it yields the protohydrate of the acid,  $\text{HO}$ ,  $\text{PO}_5$ , which is distinguished from the other hydrates by its power of coagulating the albumen of white of egg. Acetic acid does not coagulate albumen, neither does a solution of metaphosphate of soda; but if the two solutions be mixed, the acetic acid liberates metaphosphoric acid, and the albumen becomes coagulated. Metaphosphate of soda is capable of combining with water of crystallization, and retains 1 equivalent if dried at  $212^\circ$ ; this water is not basic, for on again dissolving the salt, it gives the usual reactions of the metaphosphates. If however the salt be heated to  $300^\circ$ , it does not lose weight, but becomes converted into the acid pyrophosphate of soda, the water by the application of heat having changed its function in the salt, and having now become basic.



This change of properties in the salt, without any change in the proportions of its components, here admits of a satisfactory explanation; and it is a striking and instructive illustration of the facility with which chemical compounds, by a change in molecular constitution, may sometimes give rise to substances, the properties of which may be very different, though the results of their analysis in 100 parts may numerically coincide.

Metaphosphate of soda forms with salts of baryta a white insoluble metaphosphate of baryta,  $\text{BaO}$ ,  $\text{PO}_5$ ; but when boiled, it gradually dissolves, and assimilates 2 equivalents of water, becoming converted into the acid tribasic phosphate of baryta,  $(\text{BaO}$ ,  $2 \text{HO}$ ,  $\text{PO}_5)$ . The compounds of this hydrate of phosphoric acid are all monobasic. Their solutions feebly redden litmus.

The aqueous solution of the protohydrate of phosphoric acid, when boiled, becomes converted into the tritohydrate, consequently it cannot be concentrated by the action of heat: but the solution may be preserved at common temperatures without change.

Most of the preceding facts relating to the phosphates are drawn from the important investigations of Mr. Graham (*Phil. Trans.* 1833).

*Modifications of Metaphosphoric Acid.*—Fleitmann and Henneberg (Liebig, *Ann.* lxx. 324) have described two new classes of phosphates intermediate between the metaphosphates and pyrophosphates. By melting pyrophosphate and metaphosphate of soda together, in the proportion of an equivalent of each, they obtained a salt consisting of  $(3 \text{ NaO}, 2 \text{ PO}_5)$ ; and by fusing 4 equivalents of the metaphosphate of soda with 1 of the pyrophosphate, a definite soda salt was obtained, which consisted of  $(6 \text{ NaO}, 5 \text{ PO}_5)$ ; both these salts are very unstable, and in solution pass quickly into a mixture of pyrophosphate and metaphosphate. Definite salts of silver and of magnesia corresponding to these compounds were obtained.

If the glassy metaphosphate of soda be fused, and allowed to cool very slowly, it furnishes a beautiful crystalline mass, which, when dissolved in a small quantity of hot water, forms a liquid which divides into two strata; the smaller of these contains unchanged metaphosphate of soda; but the bulk of the liquid is a solution of the crystalline salt, which may be obtained on evaporation; this solution is neutral and has a saline taste, whilst that of the ordinary or vitreous metaphosphate is insipid. The crystalline salt, by boiling, is rapidly converted into the *acid* common phosphate  $(\text{NaO}, 2 \text{ HO}, \text{PO}_5)$ ; a silver salt, consisting of  $3 (\text{AgO}, \text{PO}_5) + 2 \text{ HO}$ , may be obtained from the crystalline soda salt by precipitation.

Mr. Maddrell obtained a series of monobasic metaphosphates which were anhydrous, crystalline, and insoluble in water, but soluble in oil of vitriol. They were formed by heating a solution of the sulphate, or nitrate of the base with an excess of phosphoric acid, until the sulphuric or other acid of the salt was expelled. Salts of potash, soda, alumina, copper, nickel, &c., were thus procured. The soda salt, if prepared with phosphoric acid which contains magnesia, or any base isomorphous with it, forms an insoluble double metaphosphate. The magnesian salt is crystalline, and consists of  $3 (\text{MgO}, \text{PO}_5) + \text{NaO}, \text{PO}_5$ .

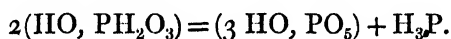
(373) PHOSPHOROUS ACID,  $(\text{PO}_3)$ ; *Eq.*, 56.—This body is pro-

duced by the slow combustion which occurs when phosphorus is left exposed to the action of the atmosphere; this may be safely effected by placing sticks of phosphorus separately in tubes open at both ends, the lower aperture of the tube being a little contracted to prevent the phosphorus from falling out; a number of these tubes are then placed in a funnel, and the dense acid liquid which forms gradually drains into a vessel placed for its reception. In this process phosphorous acid is first produced; the acid being deliquescent, attracts moisture from the air, and then by gradually absorbing oxygen, it forms phosphoric acid. The oxidation never proceeds so far as to convert the whole into phosphoric acid; the liquid therefore contains a mixture of phosphorous and phosphoric acids. To obtain a pure hydrated phosphorous acid, a stream of chlorine is sent very slowly through a deep layer of phosphorus melted under water, so that each bubble of gas shall be completely absorbed by the phosphorus; trichloride of phosphorus,  $\text{PCl}_3$ , is formed, and is immediately decomposed by the water into hydrochloric and phosphorous acids;  $\text{PCl}_3 + 3 \text{HO} = \text{PO}_3 + 3 \text{HCl}$ . The acid liquid is concentrated by a heat not exceeding  $400^\circ$ ; hydrochloric acid is expelled, and hydrated phosphorous acid is obtained in deliquescent rectangular prisms,  $(2 \text{HO}, \text{PO}_3, \text{HO})$ . When exposed to the air it gradually absorbs oxygen; and by a high temperature it is decomposed into phosphoric acid and phosphuretted hydrogen (376).

To prepare the acid in the anhydrous state it is necessary to burn phosphorus in a limited current of dry air; it is thus obtained as a white, volatile, uncrystalline, inflammable, deliquescent powder. Phosphorous acid is dibasic; that is, its salts when neutral contain 2 equivalents of base; but M. Wurtz finds that hydrated phosphorous acid, besides its two basic equivalents of water, retains a third equivalent of water, which is essential to it. Neutral phosphite of soda, for instance, consists of  $(2 \text{NaO}, \text{PHO}_4 + 10 \text{HO})$ ; when heated to  $572^\circ$ , it still retains 1 equivalent of water, and consists of  $2 \text{NaO}, \text{PHO}_4$ . Acid phosphites may also be formed: the acid phosphite of baryta, dried at  $212^\circ$  consists of  $(\text{BaO}, \text{HO}, \text{PHO}_4)$ . The acid phosphites when heated emit hydrogen gas, whilst a monobasic phosphate remains behind; thus  $(\text{BaO}, \text{HO}, \text{PHO}_4)$  becomes  $\text{BaO}, \text{PO}_5 + 2 \text{H}$ . If the phosphite contain a smaller quantity of water, phosphuretted hydrogen is also emitted; for instance, in the case of phosphite of lead  $5 (2 \text{PbO}, \text{PHO}_4) = 10 \text{PbO}, 4 \text{PO}_5 + \text{H}_3 \text{P} + 2 \text{H}$ .

(374) HYPOPHOSPHOROUS ACID,  $(\text{PO})$ ; *Equivalent*, 40; or

as is more probable,  $\text{HO}, \text{PH}_2\text{O}_3$  (Wurtz). — This compound was formerly considered to be an acid of phosphorus with a still smaller quantity of oxygen than the preceding, but it has never been obtained in the anhydrous form. In a hydrated condition it may be procured by Rose's method of boiling phosphorus with baryta in water. Phosphuretted hydrogen escapes, and on evaporation a baryta salt is obtained, composed of  $\text{BaO}, \text{PH}_2\text{O}_3$ , owing to the following decomposition:  $3 \text{BaO} + 4 \text{P} + 9 \text{HO} = 3(\text{BaO}, \text{PH}_2\text{O}_3) + \text{H}_3\text{P}$ ; and on adding sulphuric acid cautiously, pure hypophosphorous acid is obtained in solution, whilst the baryta is separated as sulphate of baryta. Hypophosphorous acid forms an uncrystallizable syrup, which has a sour, bitterish taste; its acid properties are but feebly marked, and its solution gradually absorbs oxygen from the air. When heated it first loses water; and by a stronger heat it is decomposed, and emits phosphuretted hydrogen, whilst phosphoric acid is set free: for example,



Owing to the partial decomposition of the phosphuretted hydrogen, a little phosphorus is generally deposited at the same time, and a corresponding quantity of hydrogen is liberated.

The researches of Dulong, of Rose, and especially of Wurtz (*Ann. de Chimie*, III. vii. 35, and xvi. 191), have shown that all the hypophosphites retain 2 equivalents of water, which are essential to their composition; the acid requires one equivalent of base for its saturation. The baryta salt, for example, may be represented as  $\text{BaO}, \text{PH}_2\text{O}_3$ ; and hypophosphite of lead as  $\text{PbO}, \text{PH}_2\text{O}_3$ . They correspond therefore to the monobasic phosphates, but 2 equivalents of hydrogen have taken the place of 2 equivalents of oxygen in the phosphoric acid. The hypophosphites are all soluble in water, and those of the alkalis dissolve also in alcohol: many of them crystallize easily; the crystallized salts may be preserved unchanged, but their solutions when evaporated at a high temperature, are gradually converted into phosphates by absorption of oxygen. Like phosphorous acid they reduce gold and silver from their salts. Hypophosphorous acid is distinguished from phosphorous acid by a remarkable reaction with the salts of copper; if to an excess of free hypophosphorous acid a solution of sulphate of copper be added, and the liquid be warmed to about  $130^\circ \text{F.}$ , a solid insoluble hydride of copper ( $\text{Cu}_2\text{H}$ ) precipitates. On raising the liquid to the boiling point, this hydride is decomposed into hydrogen gas and metallic copper.



(375) OXIDE OF PHOSPHORUS, ( $P_2O$ ).—A still lower degree of oxidation of phosphorus exists, which possesses neither acid nor alkaline properties. It always forms in small quantity when phosphorus is burned in air, and is one of the constituents of the red residue after the combustion has terminated. It is not however a compound of any importance. Oxide of phosphorus has neither smell nor taste, and is quite insoluble in water.

(376) PHOSPHIDES OF HYDROGEN.—The compounds of phosphorus with hydrogen are not possessed of acid characters: they are three in number: viz.  $H_3P$ ;  $H_2P$ ; and  $HP_2$ . The first is gaseous, the second liquid, and the third solid, at ordinary temperatures.

PHOSPHURETTED HYDROGEN GAS, ( $H_3P$ ); *Equivalent*, 35; *Specific Gravity*, 1.185; *Combining Volume*, 4. — Phosphuretted hydrogen is a highly inflammable colourless gas, with a fœtid alliaceous odour; it is slightly soluble in water; when transmitted through certain metallic solutions, such as those of copper or of mercury, it is absorbed and decomposed; phosphides of the metals are produced and are precipitated. When the gas is pure it is wholly absorbed by a solution of chloride of lime. A mixture of the gas with air or with oxygen explodes at a temperature of  $300^\circ$ , or sometimes even at common temperatures, if the pressure be suddenly diminished. In this gas, 1 volume of the vapour of phosphorus and 6 volumes of hydrogen are condensed into the space of 4 volumes. Its combining volume is therefore the same as that of ammonia, to which it is analogous in composition; but it does not exhibit any marked alkaline properties. Some indication of a basic character is, however, shown by it, as it combines with certain of the acids in definite proportions. For example, its compound with hydriodic acid ( $H_3P$ , III) is formed by the union of equal volumes of the two gases; it crystallizes in cubes, which fuse at a moderate heat, and if air be excluded, it may be sublimed without alteration. These crystals are deliquescent, and are decomposed by water into hydriodic acid and phosphuretted hydrogen gas. This compound is easily prepared by introducing into a small retort 127 parts of dry iodine ground up with powdered glass, and 32 parts of phosphorus in small fragments; then adding 20 parts of water; the vapours which come off consist of this compound mixed with an excess of hydriodic acid; the hydriodate of phosphuretted hydrogen condenses in crystals in the neck of the retort, if it be kept cool.

Phosphuretted hydrogen likewise combines with the perchlorides of many of the metals, such as those of tin, titanium, antimony

and iron. These compounds are decomposed, by water with escape of phosphuretted hydrogen gas.

*Preparation.*—Phosphuretted hydrogen gas may be obtained in a state of purity by the decomposition of hydrated phosphorous acid by heat;  $4(2\text{HO}, \text{PHO}_2) = 3(3\text{HO}, \text{PO}_2) + \text{H}_3\text{P}$ .

This gas, however, is generally prepared by heating fragments of phosphorus with a strong solution of hydrate of potash, or with cream of lime; hypophosphite of the base is formed, with extrication of phosphuretted hydrogen;  $\text{P}_4 + 9\text{HO} + 3\text{KO} = 3(\text{KO}, \text{PH}_2\text{O}_3) + \text{H}_3\text{P}$ . The gas so obtained has the remarkable property of spontaneously taking fire in atmospheric air or in oxygen gas; if allowed to escape into the air in bubbles, each bubble as it breaks produces a beautiful white wreath of phosphoric acid, composed of a number of ringlets revolving in vertical planes around the axis of the wreath itself, as it ascends; thus tracing before the eye, with admirable distinctness, the rapid gyratory movements communicated to the superincumbent air by the bursting of a bubble of any kind upon the surface of a still sheet of water. If the bubbles be allowed to rise into a jar of oxygen, a brilliant flash of light, attended with a slight concussion, occurs each time a bubble of the gas bursts within the jar. Owing to the spontaneous inflammation of the gas it should (to avoid danger) always be made in small vessels containing but little atmospheric air. Mr. Graham has shown that the addition of small quantities of the vapour of some inflammable bodies, such as ether, naphtha, and turpentine, destroy this self-lighting power; and that porous bodies, such as charcoal, also remove it. On the other hand, the gas obtained from phosphorous acid is not self-lighting, but the addition of so small a quantity as  $\frac{1}{100,000}$ th of its bulk of nitrous acid gas, confers this property upon it.

(377). *Liquid Phosphide of Hydrogen*,  $\text{H}_2\text{P}$ , or  $\text{H}_{10}\text{P}_5$ .—The singular property of spontaneously igniting when mixed with free oxygen which phosphuretted hydrogen possesses in certain cases, long remained without explanation, as a careful analysis indicated little or no difference in composition between the self-lighting gas and the other variety which does not possess this property. M. P. Thénard has lately shown that the self-lighting power depends upon the presence of a minute quantity of the vapour of another phosphide of hydrogen,  $\text{H}_{10}\text{P}_5$ , which takes fire the instant that uncombined oxygen is presented to it (*Ann. de Chimie*, III. xiv. 5). At ordinary temperatures this compound exists as a volatile yellowish liquid, which by exposure to light is decomposed into a

yellow, solid, and but slightly inflammable phosphide,  $\text{HP}_2$ , and into the non-self-lighting gas,  $\text{H}_3\text{P}$ ; for  $\text{H}_{10}\text{P}_5 = \text{HP}_2 + 3\text{H}_3\text{P}$ . It had long been remarked, although analysis showed no difference between the self-lighting and the common gas, that when the former was exposed to sunlight for a few hours, traces of a solid yellow compound were deposited, whilst the gas lost its self-lighting power; and that this power was also destroyed by exposing the gas to a great degree of cold. This effect is evidently due in the case of the exposure to sunlight, to decomposition of the inflammable compound, and in the case of the application of cold, to its condensation into the liquid form.

Liquid phosphide of hydrogen may be prepared by conducting the gas which is disengaged by the action of water upon phosphide of calcium ( $\text{Ca}_2\text{P}$ ), through a bent tube immersed in a freezing mixture of ice and salt; a colourless liquid of high refracting power is thus condensed. It takes fire the instant that it comes into contact with air, and burns with the intense white light of phosphorus. Solar light quickly decomposes it into the solid phosphide,  $\text{HP}_2$ , and into the gaseous phosphuretted hydrogen. If a little of the vapour of this liquid be allowed to diffuse itself through hydrogen, carbonic oxide, or any other combustible gas, it confers upon it the property of taking fire spontaneously when mixed with atmospheric air or oxygen.

(378) *Solid Phosphide of Hydrogen* ( $\text{HP}_2$ ).—The liquid phosphide is immediately decomposed by hydrochloric acid; and the solid yellow phosphide of hydrogen is formed. This substance is readily prepared by treating phosphide of calcium (538) with hot hydrochloric acid. It is insoluble in water or alcohol. When heated with potash the compound dissolves, and phosphuretted hydrogen gas is liberated. There appear to be two varieties of the solid phosphide, one of a yellow, the other of a green colour; they do not differ from each other in composition. The solid yellow hydride of phosphorus takes fire at about  $300^\circ \text{F}$ .

(379) *CHLORIDES OF PHOSPHORUS*.—With chlorine phosphorus forms two compounds, a terchloride  $\text{PCl}_3$ , corresponding to phosphorous acid, and a pentachloride,  $\text{PCl}_5$ , which corresponds to phosphoric acid. So strong is the affinity between these elements, that in an atmosphere of chlorine phosphorus immediately takes fire.

*Terchloride of Phosphorus*, ( $\text{PCl}_3$ ); *Eq.*, 138.5—This liquid may be obtained by transmitting a gentle stream of perfectly dry chlorine gas through dry and melted phosphorus contained in a retort; the chloride distils as a very volatile, transparent, colourless liquid, of

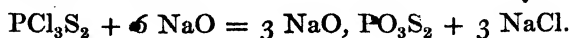
a specific gravity of 1·616, at 32°; it fumes in air, and boils at 173°·4. It dissolves phosphorus freely. It is immediately decomposed by a large excess of water, and forms phosphorous and hydrochloric acids;  $\text{PCl}_3 + 3\text{HO} = \text{PO}_3 + 3\text{HCl}$ .

Tetrachloride of phosphorus is often prepared by transmitting the vapour of phosphorus over corrosive sublimate placed in a long tube, and gently heated.

*Pentachloride of Phosphorus*, ( $\text{PCl}_5$ ); *Eq.*, 209·5.—This compound is obtained by placing dry phosphorus in a flask provided with a stopcock, exhausting the air, and allowing chlorine to enter so long as it is absorbed; or it may be formed by treating sesquichloride of phosphorus in a tall glass with an excess of chlorine: it forms a white crystalline solid, which volatilizes below 212° whilst still solid, but it may be fused under pressure; its boiling point, according to Mitscherlich, is 296° F. In the flame of a lamp it burns, producing chlorine and phosphoric acid; with ammonia it combines readily. It is very deliquescent, and by a large excess of water is immediately decomposed into phosphoric and hydrochloric acids;  $\text{PCl}_5 + 5\text{HO} = \text{PO}_5 + 5\text{HCl}$ .

If the vapour of water be allowed slowly to mingle with that of the pentachloride, hydrochloric acid and an *oxychloride of phosphorus*,  $\text{PCl}_3\text{O}_2$ , are gradually formed; the latter, according to Wurtz, is a limpid, volatile, fuming liquid, of sp. gr. 1·7, which boils at 230° F. Water decomposes it into phosphoric and hydrochloric acids.

With sulphuretted hydrogen pentachloride of phosphorus produces hydrochloric acid, and a *sulphochloride of phosphorus*, consisting of  $\text{PCl}_3\text{S}_2$ . It is a fuming, colourless liquid, which boils at 257°. Wurtz finds that this sulphochloride of phosphorus, if heated with a solution of caustic soda in excess, exchanges its chlorine for oxygen; chloride of sodium forms, and a *sulphoxyphosphate of soda* may be obtained in six-sided tabular crystals which contain 24 equivalents of water. The composition of this salt is analogous to that of the tribasic phosphate of soda, but the two are not isomorphous. The following equation explains the changes which accompany its production:—



One half of the soda is decomposed, imparting its oxygen to the sulphochloride, from which it receives a corresponding amount of chlorine.

(380) IODIDES OF PHOSPHORUS.—Two iodides of phosphorus

may be formed, a biniodide and a teriodide (Corenwinder, *Ann. de Chimie*, III. xxx. 242). The biniodide,  $(PI_2)$ ; *Equivalent*, 286, may be obtained by dissolving 1 equivalent of phosphorus in bisulphide of carbon and adding 2 equivalents of iodine: by cooling the mixture artificially, thin flexible prismatic crystals of the iodide are deposited of a bright orange colour. They melt at  $230^\circ$ , and are decomposed by water, hydriodic acid being one of the products.

*Teriodide of Phosphorus*,  $(PI_3)$ ; *Eq.*, 413.—This compound may be obtained in a similar manner to the last, viz., by dissolving the proper proportions of the two elements in bisulphide of carbon; the liquid is concentrated by evaporation, and on cooling it by a freezing mixture, dark red six-sided plates are formed; it melts between  $120^\circ$  and  $130^\circ$  F., and on cooling crystallizes in fine prisms. It deliquesces rapidly when exposed to the air.

Mr. Brodie (*Quart. Journ. Chem. Soc.*, V. 289) finds that iodine, when heated with phosphorus in the proportion of 1 equivalent of iodine to 100 equivalents of phosphorus, converts nearly the whole of the phosphorus into the red variety described by Schrötter. When phosphorus was placed in a long tube, and heated till it just melted, and iodine was projected gradually into the phosphorus, the iodine dissolved, colouring the phosphorus slightly red; when heated by an oil bath to  $212^\circ$ , the colour became deep red, and between  $250^\circ$  and  $266^\circ$ , a scarlet powder was deposited on the sides of the tube; at  $284^\circ$  the mass was quite solid, and on raising the heat to  $392^\circ$  F., a sharp explosion took place; a sudden evolution of heat occurred, and the cork which closed the tube was blown out by the vapour of phosphorus. The red mass may be distilled in closed tubes, and when it condenses in the cooler portions of the tubes it is still in the red modification. Mr. Brodie considers the changes which occur in this process to be the following; first, the formation of biniodide of phosphorus, next the transformation of this iodide by heat into an allotropic iodide, and thirdly, the decomposition of the new iodide into red phosphorus and a volatile iodide, which acts upon a further portion of the phosphorus; and thus the action is indefinitely continued.

(381) PHOSPHIDE OF NITROGEN ( $N_2P$ ?).—If terchloride of phosphorus be cooled by a freezing mixture, and saturated with ammoniacal gas, a white saline mass is obtained; it is to be introduced into a tube of Bohemian glass, and heated to redness in a current of dry carbonic acid as long as any sal ammoniac sublimes; a yellowish-white bulky amorphous powder remains behind: this substance is Rose's phosphide of nitrogen. In close vessels it sustains a red heat without fusion or volatilization, but when heated in air it is

slowly oxidized, with formation of phosphoric acid, and if projected into fused hydrate of potash, it is decomposed with incandescence; phosphate of potash being formed, whilst ammonia and nitrogen are disengaged; but it is remarkable that dry chlorine, and hydrochloric acid-gases, and the vapour of sulphur, are without action upon it, even at a red heat; and it is but very slowly attacked by concentrated nitric acid. Solutions of the alkalis exert scarcely any action upon it. When heated in hydrogen, ammonia is formed. It combines with sulphuretted hydrogen, and if heated in a current of the gas it slowly sublimates in the form of a white powder. According to Gerhard, however, the so-called phosphide of nitrogen contains hydrogen, and is really  $\text{HN}_2\text{P}$ .

(382) **SULPHIDES OF PHOSPHORUS.**—Sulphur and phosphorus may be melted together in all proportions: several definite compounds exist between them, and, according to the researches of Berzelius, these compounds correspond in composition with the oxides of phosphorus; and in addition to these, a compound,  $\text{PS}_{12}$ , may be formed. All the sulphides of phosphorus are more fusible than either element separately, and are exceedingly inflammable: most of them crystallize. They combine with the alkaline sulphides, and form a series of definite salts.

The combination of sulphur with phosphorus should be gradually effected under warm water; great heat is extricated by their union, and the experiment requires to be conducted very carefully, in order to avoid explosion.

## CHAPTER VIII.

### SILICON AND BORON.

#### § I. SILICON, OR SILICIUM.

*Symbol, Si; Equivalent, 14.24.*

(383) **SILICON** when in combination with oxygen is the most abundant solid constituent of the earth's crust. To obtain the element in its uncombined form, fluorspar and fine quartzose sand, or ground flints, are heated with concentrated sulphuric acid; a gaseous fluoride of silicon is formed, which partially dissolves in water, producing an acid solution. This acid liquid, when neutralized with a solution of potash, yields a sparingly soluble salt ( $\text{KF}$ ,  $\text{SiF}_2$ ). This silicofluoride of potassium is to be thoroughly

dried, and mixed in a glass or iron tube with eight or nine-tenths of its weight of potassium, and heated. Fluoride of potassium is formed, whilst silicon is reduced and partially combined with the excess of potassium;  $(\text{SiF}_2 + \text{KF}) + 2 \text{K} = 2 \text{Si} + 3 \text{KF}$ . The mass, when cold, is treated with cold water, which produces a copious extrication of hydrogen gas, owing to the decomposition of the water by the excess of potassium. The washing with cold water is continued so long as any alkaline reaction upon test paper is observed; when this ceases, it may finally be well washed with boiling water, as long as anything dissolves. Silicon may also be obtained by heating potassium in a glass tube in a current of the vapour of chloride of silicon.

Silicon so obtained is a dull brown powder, insoluble in water, in which it sinks. It is a non-conductor of electricity; it soils the fingers when touched; it is not acted upon by nitric or sulphuric acid, but dissolves readily in hydrofluoric acid, and in a warm solution of potash. When heated in air or in oxygen it burns brilliantly, and is converted into silica, which is the only known oxide of silicon: the intense heat emitted causes the silica to fuse and form a superficial coating over the unburnt silicon. Silicon has never been fused nor volatilized.

The brown powder just described, if heated intensely in a closed platinum crucible, parts with a trace of hydrogen, shrinks greatly, becomes much denser and darker in colour, and undergoes a remarkable change in properties. After such ignition, the silicon (which Berzelius distinguishes as  $\text{Si}_\beta$ ) may be heated strongly in air or in oxygen, even when urged in the blowpipe flame, without taking fire; it has become sufficiently heavy to sink in oil of vitriol, and it resists the action of pure hydrofluoric acid, although if treated with a mixture of nitric and hydrofluoric acids it is rapidly dissolved. It may even be fused with nitre or with chlorate of potash without undergoing oxidation; but if the heat be urged to whiteness, the silicon burns brilliantly in the nitre; the oxidation, however, is much hastened by the addition of a little carbonate of potash; the mixture then deflagrates briskly, even though it may be at a much lower temperature: by fusion with carbonate of potash alone, it is easily and completely oxidized; in both cases, silica is formed, and immediately dissolves in the melted alkali. Deville (*Ann. de Chimie*, III. xliii. 31) has described a third modification of silicon, in the form of brilliant plates possessed of a metallic lustre, resembling platinum filings in appearance. It is a conductor of electricity; it may be heated to whiteness in a current of oxygen without undergoing change, but is gradually dissolved by a mixture of hydro-

fluoric and nitric acid: though it is oxidized but very slowly when fused with hydrate of potash. This form of silicon was obtained by acting with hydrochloric acid upon a silicide of aluminum, procured by the electrolytic decomposition of an impure double chloride of sodium and aluminum.

(384) SILICIC ACID, or *Silica*, ( $\text{SiO}_2$ ); *Eq.*, 30.24.—Silicon appears to form only a single oxide. Some difficulty is therefore experienced in deciding on the number of equivalents of oxygen that it contains. According to Berzelius the two elements are united in the proportion of 48.02 of silicon and 51.98 of oxygen; and the same eminent chemist represents it as a tetroxide. There are, however, reasons which render it more probable that it contains only 2 equivalents of oxygen, and that it corresponds in composition to carbonic acid: for example, one equivalent of chloride of silicon, when converted into vapour, instead of forming an exception to the general rule, as it does upon the theory of Berzelius, would then produce two volumes of vapour as usual: and in decomposing fused carbonate of soda by the addition of finely divided silica, it is found that the whole of the carbonic acid is expelled when the proportion of silica is to the carbonate as 31 to 54. Gmelin has calculated the formulæ of the natural silicates upon this supposition, and his formulæ have been adopted by Brooke and Miller in their treatise on mineralogy. This view has the advantage of greater simplicity, and it will be employed in this work. The formula for silica will therefore be  $\text{SiO}_2$ , instead of  $\text{SiO}_3$  which is given in the table at p. 18: and the equivalent of silicon is, therefore, 14.24, instead of 21.36.

Pure silica occurs crystallized in six-sided prisms, transversely striated, and terminated by six-sided pyramids, in rock crystal and in some forms of quartz. It is nearly pure in agate, flint, calcedony, and opal; it constitutes the principal ingredient of all sandstones; and it enters largely into the composition of felspar, and a vast variety of minerals. Pure silica is perfectly transparent and colourless; in hardness it approaches the precious gems; it has a specific gravity of 2.6. A heat as intense as that of the oxyhydrogen blowpipe is required for its fusion; it then melts to a transparent glass, which may be drawn out into fine, flexible, elastic threads. Native silica is insoluble in water, and in all acids except the hydrofluoric. It is not volatile when heated alone, but when heated in a current of steam it undergoes partial sublimation, and is thus frequently found in the throats of furnaces, forming concretionary nodules, somewhat resembling calcedony in appearance.



*Preparation.*—Silica presents the characters of an earth, but though insoluble it possesses feeble acid properties, as is shown by the usual process of obtaining it in a state of purity:—a mixture of carbonate of potash and soda is fused by a red heat, and ground flint or some other siliceous mineral in fine powder is added in small quantities to the melted mass; on each addition a brisk effervescence, due to the escape of carbonic acid, takes place. As soon as the addition of the mineral ceases to produce this effect no more is added, but the mixture is heated strongly for some minutes. It is then allowed to cool, and if digested in water, the mass slowly dissolves, with the exception of any impurities, such as oxide of iron, which the siliceous material may have contained. A larger quantity of silica than that above indicated would still yield a mixture which by a strong heat might be fused; but it becomes less soluble in proportion to the excess of silica, till at length a point is reached at which it is no longer soluble in water or in the common acids; indeed it forms the basis of glass. To obtain pure silica, however, an excess of alkali is always used; the resulting compound is then easily attacked by acids, in which it is wholly dissolved, if the acid be dilute and in sufficient quantity. If the solution in hydrochloric acid be evaporated, the silica separates as a gelatinous hydrate, which, by continuing the heat, forms a white earthy powder no longer soluble in acids: after being well washed with acidulated water as long as anything dissolves, and then dried and ignited, it is perfectly pure. In this form silica, like charcoal and other porous bodies, rapidly absorbs aqueous vapour from the air, without becoming sensibly moist. Whilst in this extreme state of subdivision, its particles, when heated, exhibit a singular mobility; they flow almost like a liquid when the crucible containing them is inclined, and they are scattered by the least breath of air. Perfectly pure silica may also be procured by transmitting the gaseous fluoride of silicon into water; part of its silica is deposited in white flocculi, which, if washed and ignited, yield silica of snowy whiteness. Silica may likewise be obtained nearly pure by heating colourless quartz to redness, and quenching it in water; the mineral by this treatment becomes friable, and is then easily reduced to a fine powder: common flints treated in a similar manner give a very white powder, which is nearly pure silica.

(385) *Hydrates of Silicic Acid.*—Insoluble however as silica generally appears in water, a modification of it exists which dissolves completely, though sparingly. When dissolved it furnishes a tasteless solution, which does not redden litmus; and when evaporated

at a gentle heat, the solution leaves a semi-transparent mass, which by further desiccation crumbles to a white powder. This white powder is generally stated to be soluble in dilute acids; but M. Doveri (*Ann. de Chimie*, III. xxi. 47) has shown that this is an error, arising from the perfect transparency which the hydrate of silica assumes when treated with dilute acids. If the solution be filtered, nearly the whole of the silica remains on the filter in the form of a transparent jelly. Silica, in fact, when once deposited, even in the gelatinous form, is almost insoluble either in water or in acids; but a large amount of silica dissolves, in certain cases, at the moment of its liberation from some of its compounds which are already in solution. For instance, if a dilute solution of an alkaline silicate be poured into a considerable excess of hydrochloric acid, the whole of the silica is retained in solution: but from this acid solution it may be precipitated by the gradual addition of potash, so as to neutralize the acid: and if to a solution of an alkaline silicate in water hydrochloric acid be gradually added, the silica precipitates in a gelatinous form in proportion as the alkali is neutralized.

According to the experiments of M. Doveri, gelatinous silica, if dried at the ordinary temperature of the air, in vacuo over sulphuric acid, retains about 17 per cent. of water, which corresponds to the sesquihydrate,  $2\text{HO}, 3\text{SiO}_2$ . If dried at  $212^\circ$ , half this quantity of water is expelled, and a definite hydrate ( $\text{HO}, 3\text{SiO}_2$ ) is left; but at  $700^\circ\text{F}$ . it becomes anhydrous. The sesquihydrate may even be obtained in a crystalline form. In order to effect this, a solution of silicate of potash is mixed with one of sulphate of copper; a precipitate, consisting of silicate of copper and of hydrate of silica, is formed; after washing the precipitate by decantation, it is treated with hydrochloric acid, which dissolves the silicate of copper; the liquid is filtered from a portion of undissolved silica. On transmitting a current of sulphuretted hydrogen through the filtered liquid the copper is wholly precipitated as sulphide, whilst the solution retains pure silica dissolved in hydrochloric acid: the excess of sulphuretted hydrogen is easily expelled by heat. The hydrochloric solution of silica, if placed in vacuo over quick lime, as it evaporates yields sesquihydrate of silica, partly in the form of a white amorphous powder, but chiefly in that of radiated tufts of plates, or needle-shaped crystals, which are transparent, and possess a high lustre.

Mr. Way (*Quart. Journ. Chem. Soc.* vi. 102) has recently called attention to the existence of beds situated at the base of the chalk

formation, between the upper greensand and the gault, which contain a large proportion of silica in the hydrated condition: the proportion of hydrated silica in these deposits varies very greatly, ranging from 5 to as much as 72 per cent., being most abundant in the upper portion of the deposit.

Insoluble silicic acid may be gradually converted into the soluble variety by long digestion with solutions of the alkalis. Even flints in their unground condition may be dissolved in strong solutions of caustic alkali, if the solution be digested upon them under pressure at a temperature of between  $300^{\circ}$  and  $400^{\circ}$  F. The very concentrated solution of silicate of potash or of soda of glairy consistence which may thus be formed, has been used by Mr. F. Ransome, of Ipswich, as a cement for consolidating siliceous sand into an artificial stone:—finely divided siliceous sand, mixed with suitable colouring material, is moistened with this cement, and pressed into moulds; after gradual drying the mass is fired: at a high temperature the silicate becomes semivitrified, and agglutinates the grains of sand; a very hard, durable, artificial sandstone, which previous to being fired can be moulded into any desired form, is thus obtained. Finely divided hydrate of silica is also dissolved by the alkaline carbonates: the carbonates are only partially decomposed by the silica that dissolves. It appears to be owing to the solubility of silica in solutions of the carbonates that almost all spring and river waters contain silica in solution in minute quantity; on evaporation the silica is obtained in the insoluble form. When the action of the alkaline liquid is aided by that of a high temperature, as is the case with the Geysers, or boiling springs of Iceland, very large quantities of silica are dissolved, which, as the liquid cools, are deposited as 'petrifications' on surrounding objects exposed in the basin or in the stream.

Silica also exists in the soluble form in a class of minerals termed zeolites, which are hydrated siliceous compounds (571) found in the cavities of the amygdaloid rocks. The zeolites, if finely powdered, and treated with hydrochloric acid, swell up to a transparent jelly; this gelatinous mass is the hydrate of silica.

These observations on the various conditions under which silica may be rendered soluble derive their interest from the extensive formation of crystallized silica, so abundantly diffused over the surface of the earth. The zeolites may have been obtained by deposition from solution; calcedony possibly by spurious sublimation; quartz and agate by crystallization from an aqueous solution.

•(386) *Silicates*.—The silicates are most abundant natural productions. All the forms of clay, felspar, mica, hornblende, and a

large number of other common minerals, are compounds of this description.

Silica combines with bases in several different proportions; most of its compounds are found in the form of crystallized minerals, many of which are double silicates of very complex composition. The combinations with bases which are of most usual occurrence belong to one or other of the following classes:—

	Examples.	Formulae.
$2 \text{ MO}, 3 \text{ SiO}_2$ , or Sesquisilicates	$\left\{ \begin{array}{l} \text{Silicate of lime} \\ \text{Meerschau, (hy-} \\ \text{drated silicate of} \\ \text{magnesia)} \end{array} \right\}$	$\left\{ \begin{array}{l} 2 \text{ CaO}, 3 \text{ SiO}_2 \\ 2 \text{ MgO}, 3 \text{ SiO}_2 + 2 \text{ HO} \end{array} \right.$
$\text{MO}, \text{SiO}_2$ Neutral silicates	$\left\{ \begin{array}{l} \text{Wollastonite, (sili-} \\ \text{cate of lime)} \\ \text{Diopase, (hydrated} \\ \text{silicate of copper)} \end{array} \right\}$	$\left\{ \begin{array}{l} \text{CaO}, \text{SiO}_2 \\ \text{CuO}, \text{SiO}_2 + \text{HO} \end{array} \right.$
$2 \text{ MO}, \text{SiO}_2$ Dibasic silicates	$\left\{ \begin{array}{l} \text{Olivine} \\ \text{Iron forge cinder} \end{array} \right\}$	$\left\{ \begin{array}{l} 2 (\text{Mg, Fe}) \text{O}, \text{SiO}_2 \\ 2 \text{ FeO}, \text{SiO}_2 \end{array} \right.$
$\text{MO}, 2 \text{ SiO}_2$	$\left\{ \begin{array}{l} \text{Bisilicates. The composition of many of the ordinary varieties} \\ \text{of glass may be approximatively represented by mixtures of} \\ \text{different silicates which have this formula} \end{array} \right.$	

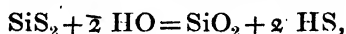
In the above formulæ, MO stands for 1 equivalent of any metallic protoxide, such as lime, magnesia, or protoxide of iron.

Most of the silicates are fusible; their fusibility increases by mixture with each other; those which contain readily fusible oxides melt at the lowest temperature, and in general the basic silicates fuse more readily than those which are neutral in composition, or which contain excess of acid. All the silicates are insoluble in water, with the exception of silicates of the alkalies which contain a large amount of base. The hydrated silicates, and those which contain the largest proportion of base, are those most easily decomposed by acids; but the anhydrous neutral and acid silicates of the earths are not decomposed by any acid except the hydrofluoric. The silicates may be detected by fusing them with carbonate of soda or of potash, and then heating the residue with acid, and evaporating to dryness; on treating what is left with hot water, the silica remains undissolved in the form of a white powder, which, when fused with carbonate of soda upon platinum foil before the blowpipe, yields a colourless bead of glass.

The acid character is so feebly marked in silica, that the ordinary vegetable acids, such as the acetic, oxalic, and the tartaric, precipitate silica from its combinations with the alkalies; and a current of carbonic acid gas, or even the gradual absorption of carbonic acid from the atmosphere, produces a similar result. At a high temperature, however, the action is reversed; for as silica is not volatilized to any perceptible extent by the heat of a furnace, it

decomposes the carbonates and the salts of all the volatile acids when ignited with them; thus even the sulphates yield up their bases to the silica, whilst the sulphuric acid is expelled.

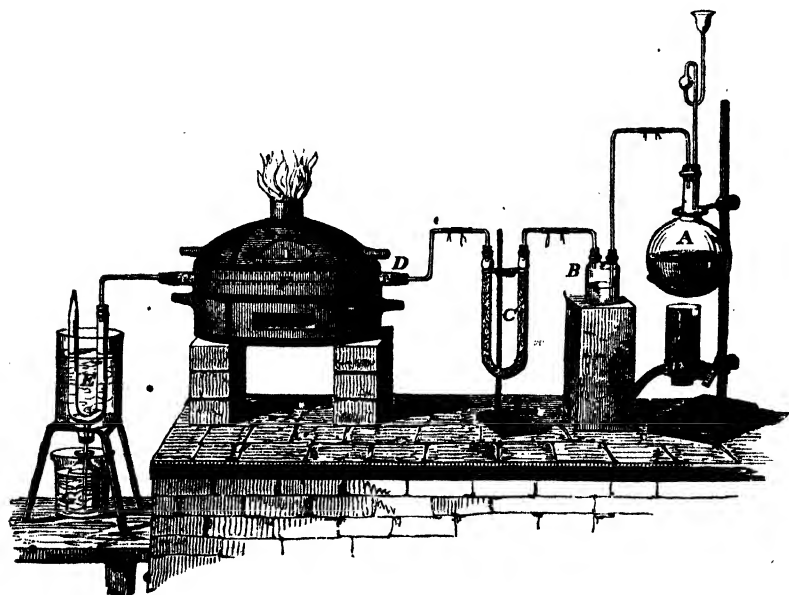
(387) **SULPHIDE OF SILICON**,  $\text{SiS}_2$ ; *Equivalent*, 46.24.—A sulphide corresponding in composition to silicic acid is formed by transmitting the vapour of bisulphide of carbon over a mixture of finely divided silica and carbon: and when either compact or pulverulent silicon is strongly heated in an atmosphere of sulphur, combustion occurs with a red glow, and a white earthy looking sulphide, which rapidly absorbs moisture from the air, is the result: it is completely soluble in water, but it is decomposed as it dissolves, in the manner shown in the following equation:—



sulphuretted hydrogen and soluble silica being formed: the latter may be obtained as a jelly by evaporation.

(388) **CHLORIDE OF SILICON**,  $(\text{SiCl}_2)$ ; *Eq.*, 85.24; *Combining volume as vapour*, 2.—This compound may be formed by heating silicon in chlorine, or more economically by the following indirect method. Finely powdered silica is made up into a paste with oil and charcoal, heated in a covered crucible, and the charred mass in fragments is transferred to a porcelain tube, ignited and subjected to a current of dry chlorine: neither chlorine nor carbon separately can

FIG. 271.



decompose silica, but together they effect it easily; carbonic oxide escaping, whilst chloride of silicon is formed;  $\text{SiO}_2 + \text{Cl}_2 + 2 \text{C} = 2 \text{CO} + \text{SiCl}_2$ . The product is received into vessels cooled with a freezing mixture. Fig. 271 shows a form of apparatus by which the chloride may be readily prepared: *D* is a porcelain tube, which contains the mixture of charcoal and silica; chlorine is liberated from the flask, *A*, washed with water in *B*, dried by passing over pumice and sulphuric acid contained in the tube *C*, and allowed to pass through the tube *D*, which with its contents is exposed to a red heat in the furnace; the chloride of silicon distils over into the bent tube, *E*, where it is condensed by immersion in a freezing mixture of ice and salt; a tube fused into the bend of the tube *E*, conveys the chloride into a bottle, *G*, which may also be kept cool by ice.

Chloride of silicon is a transparent colourless liquid, which has a pungent, acid, irritating odour; it fumes strongly in the air, is very volatile, and boils at  $138^\circ \text{F}$ . According to Pierre, the specific gravity of the liquid at  $32^\circ \text{F}$ . is 1.5237. Its vapour has a specific gravity of 5.939. In this vapour 4 volumes of chlorine and 1 equivalent of silicon are condensed into 2 volumes. Water immediately decomposes it, depositing hydrated silica, and forming hydrochloric acid. The liquid chloride does not act on potassium, but if the metal be heated in its vapour, chloride of potassium is produced, and silicon is set free; by washing it, the latter may be procured in a state of purity. Berzelius recommends this as one of the best methods of obtaining silicon.

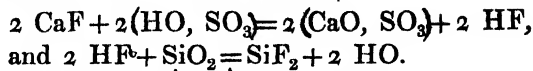
Two compounds between the sulphide and the chloride of silicon have been obtained; they may be represented by the formulæ  $(\text{SiS}_2 + 2 \text{SiCl}_2)$  and  $(2 \text{SiS}_2 + \text{SiCl}_2)$ .

*Bromide of Silicon* ( $\text{SiBr}_2$ ), is analogous in properties to the chloride: it may be formed in a similar manner.

(389) **FLUORIDE OF SILICON**, ( $\text{SiF}_2$ ); *Eq.*, 52.24; *Specific Gravity*, 3.60; *Combining Volume*, 2.—The fluoride is one of the most remarkable compounds of silicon: so powerful is the affinity between fluorine and silicon that hydrofluoric acid separates silicon from its most intimate combinations, such as silicic acid and glass.

In order to prepare the fluoride of silicon, equal parts of finely powdered fluorspar and siliceous sand, or coarsely powdered glass, are mixed in a capacious flask or retort, with 6 parts of sulphuric acid. On the application of heat, a colourless gas, with a peculiar pungent acid odour, is given off; hydrofluoric acid is libe-

rated, and this immediately attacks the silica, as is shown in the following representation of the reaction :—



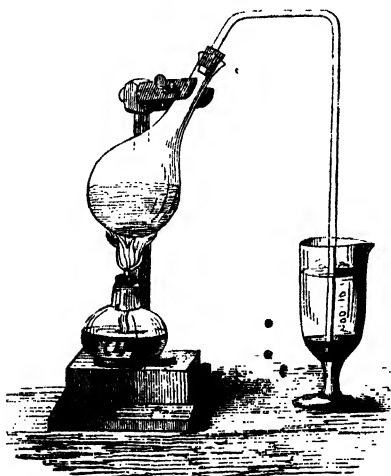
It fumes strongly in air ; it is not inflammable, but extinguishes a lighted taper ; under strong pressure it was liquefied by Faraday ; and according to, M. Natterer it becomes solid at  $-220^\circ \text{ F}$ . The gas is dissolved and partially decomposed by water, it must therefore be collected over mercury, and in jars which have been perfectly dried, at a high temperature ; the slightest trace of moisture on the surface of the jar, causes a deposition of silica, which adheres very firmly to the glass and renders it opalescent. Fluoride of silicon combines with twice its volume of ammoniacal gas, and forms with it a crystalline volatile compound.

(390) SILICOFLUORIC ACID : *Hydrofluosilicic Acid*, ( $\text{HF}, \text{SiF}_2$ ) ; *Eq.*, 72·24. — When a stream of gaseous fluoride of silicon is transmitted through water, it is partially decomposed and partially dissolved. Two equivalents of water re-act on 3 equivalents of the fluoride, and produce the silicofluoric acid, which dissolves, whilst one-third of its silicon is deposited as silicic acid :—



To prepare this acid, the tube from which the fluoride is escaping must not plunge at once into water, otherwise it will speedily become obstructed by the deposited silica. It is there-

FIG. 272.



fore necessary to place a little mercury at the bottom of the vessel to prevent the contact of water with the tube, which must dip beneath the mercury, as shown in fig. 272. Each bubble as it rises becomes surrounded by a siliceous envelope, and finally the liquid sets into a gelatinous mass : the acid liquid is separated by pressure in linen from the deposit, which when freed from adhering acid, constitutes a pure hydrate of silica.

A saturated solution of silicofluoric acid forms a very sour, fuming liquid: when dilute it produces transparent jellylike precipitates in the alkaline salts; it is frequently employed as a precipitant of potash. With salts of baryta the acid gives a white crystalline precipitate.

In solution it does not attack glass; but it does so if allowed to evaporate upon it; the fluoride of silicon volatilizes, leaving free hydrofluoric acid, which reacting on the silica produces water and fluoride of silicon, as in the ordinary process for making that gas:  $2 \text{ HF} + \text{SiO}_2 = \text{SiF}_2 + 2 \text{ HO}$ . Silicofluoric acid combines with bases to form salts, if the base be not added in excess; if an excess of base be employed, silica is precipitated, and the whole of the fluorine is separated as a metallic fluoride. In the first case the action may be thus represented:  $\text{KO} + (\text{HF}, \text{SiF}_2) = \text{HO} + (\text{KF}, \text{SiF}_2)$ . In the second case:  $3 \text{ KO} + (\text{HFF}, \text{SiF}_2) = \text{HO} + 3 \text{ KF} + \text{SiO}_2$ .

## § II. BORON.

*Symbol, B; Equivalent, 10.9.*

(391) BORON is the combustible radical of the acid contained in borax, whence it derives its name. In nature it is always met with in combination with oxygen. It is a body which occurs in comparatively sparing quantities, and only in a few localities. In its properties, and its mode of combination, it presents considerable analogy with silicon.

Boron is most advantageously obtained by a process analogous to that employed in the case of silicon. The borofluoride of potassium, a sparingly soluble salt, is made by saturating hydrofluoric with boracic acid, neutralizing by carbonate of potash, and washing the compound with cold water; it is then dried at a heat a little below redness. When cold it is mixed with an equal weight of potassium, and heated in a covered iron crucible. The fluoride of potassium is removed by hot water.  $\text{KF}, \text{BF}_3 + 3 \text{ K} = 4 \text{ KF} + \text{B}$ .

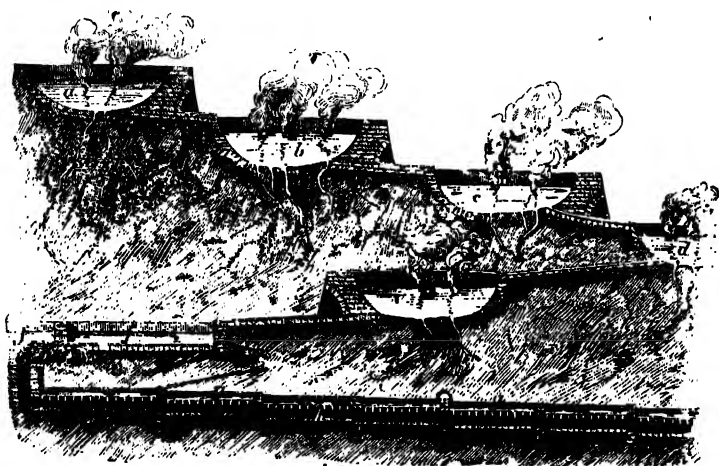
Boron is a dull olive green powder, which, before it has been strongly ignited, soils the fingers, and is dissolved by pure water in small quantity, forming a greenish yellow solution; it is, however, precipitated unchanged on adding a little solution of sal ammoniac. Boron is not acted on by exposure to air, to water, or to solutions of the alkalis, whether cold or boiling. It is, however,



easily oxidized when treated with nitric acid or with aqua regia. After exposure to intense heat in vessels from which air is excluded, it becomes denser, and darker in colour, but shows no signs of fusion or volatilization. As first obtained, boron exhibits a strong affinity for oxygen, and takes fire below redness, if heated in air or oxygen; it burns with a red light, emitting vivid scintillations: it is thus converted superficially into boracic acid, which melts and protects a portion of the boron. If mixed with nitre it deflagrates powerfully, and when fused with carbonate of potash, it decomposes the carbonic acid, setting charcoal free, and forming borate of potash. Boron, like silicon, is a non-conductor of electricity.

(392) BORACIC ACID,  $(\text{BO}_3)$ ; *Eq.* 35. — This acid, which is considered as a teroxide of boron, is the only known compound of oxygen and boron. It is found in the uncombined state in some volcanic districts, where it issues in small quantity along with the jets of steam or *fumerolles*, maintained by the action of subterranean fire. These, in some parts of Tuscany, are directed into small lagoons, or artificial basins, such as those shown in *fig.* 273,

FIG. 273.



the waters of which on evaporation yield a crude boracic acid, from which a large proportion of the borax of commerce is now manufactured. According to the ingenious suggestion of Larderello, the heat supplied by the fumerolles themselves is employed in this evaporation. Water from the adjacent springs is directed into the uppermost basin, *a*; here it stays twenty-four hours, and is run off after successive intervals of twenty-four hours into each of the

four lower basins, *b, c, d, e*. From the last of these it flows into settling vats, *f, f*, where in the course of twenty-four hours more, the suspended matters subside. The supernatant liquid is then decanted into shallow leaden evaporating pans, *g, g*, heated by the vapours of several fumerolles, which circulate underneath in flues, *h*, arranged for the purpose. In twenty-four hours the liquor is reduced to about half its bulk; it is then transferred to a smaller pan, on a lower level, where it evaporates for twenty-four hours longer: it is again transferred to a smaller pan, when after the lapse of twenty-four hours more, it is sufficiently concentrated to crystallize on cooling. Sulphate of lime in abundance is deposited in the pans during these evaporations, and it requires removal from time to time. Payen stated in 1841, that 750 tons of boracic acid are thus annually procured from Tuscany. This crude acid, however, contains only about three-quarters of its weight of the pure crystals, the remainder consisting principally of sulphate of ammonia with small quantities of sulphate of alumina, and of other alkaline and earthy sulphates, and a small proportion of silica.

The commercial acid is purified by adding carbonate of soda to saturation, and thus forming borax, which is obtained nearly pure by crystallization (494).

To obtain the acid, purified borax is dissolved in 4 parts of boiling water, and to the hot solution, oil of vitriol equal in weight to that of one-fourth of the borax employed, diluted with a little water, is added. The sparingly soluble boracic acid crystallizes out on cooling, in pearly looking scales which have a greasy feel; they contain 3 equivalents of water. In this process sulphate of soda is formed, and boracic acid is liberated. It is not however quite pure, as it always retains a little sulphuric acid. To remove this, the crystals are washed with ice-cold water; dried, and fused in a platinum crucible, and on re-dissolving it in four times its weight of boiling water, the acid, as it recrystallizes, is obtained perfectly pure.

The crystals of boracic acid effloresce and lose two-thirds of their water at a gentle heat, and at a slight increase of temperature become anhydrous; at a red heat or a little below, boracic acid fuses to a transparent, viscid, ductile glass, which remains clear as it cools. It gradually absorbs moisture from the air, and crumbles to pieces.

Boracic acid communicates to its compounds the property of ready fusibility; indeed it is chiefly on this account that it is valued. Many of the borates are admirably adapted for fluxes,

which are applied in glazes for porcelain, and in the melting of gold and silver.<sup>4</sup>

Boracic acid is sparingly soluble in cold water, but it dissolves in three times its weight of boiling water: the solution has a bitterish and scarcely sour taste; it turns turmeric paper brown, like an alkali; it gives to litmus a purplish-red tint, instead of the usual bright red of the stronger acids.<sup>5</sup> It gradually decomposes solutions of the carbonates even in the cold; but, on the other hand, a brisk current of carbonic acid or of sulphuretted hydrogen will cause a separation of boracic acid in crystals from a strong solution of borax. Boracic acid dissolves in alcohol, and the solution burns with a characteristic green flame. It is not possible to evaporate a solution of boracic acid either in alcohol or in water without losing a portion of the acid, as the vapour always carries with it an appreciable amount of the acid: if steam at a high temperature be transmitted over boracic acid the acid is volatilized in considerable quantities. It appears to be in this manner that in Tuscany the supply of acid is raised to the surface by the jets of steam which issue from the strata below (Fig. 273).

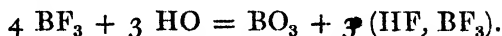
Anhydrous boracic acid is but very slowly volatilized by ignition, and hence, though an exceedingly feeble acid, it at high temperatures expels all acids more volatile than itself when fused with their salts. It enters into combination with the alkaline bases in a great variety of proportions, resembling silicic acid in this respect, as in some others. Although many of these salts contain more than 1 equivalent of acid, they all restore the colour of reddened litmus paper. A sexborate of potash ( $\text{KO}, 6 \text{BO}_3, 10 \text{aq}$ ) may be obtained in crystals, and a triborate ( $\text{KO}, 3 \text{BO}_3, 8 \text{aq}$ ) has also been crystallized. The alkaline borates are freely soluble, those of the other bases are only imperfectly soluble; none of the borates, however, are so insoluble as to furnish an accurate mode of ascertaining the quantity of boracic acid present in solution by the formation of a precipitate. All the sparingly soluble borates are dissolved by dilute nitric acid. In analysing a borate it is usual to determine the amount of all the other acids and bases, and other constituents, and to estimate the deficiency as boracic acid.

(393) A *sulphide* and a *chloride* of boron may be prepared by methods similar to those employed to obtain the corresponding compounds of silicon. The *chloride of boron* ( $\text{BCl}_3$ ), *eq.* 117.5, is gaseous at ordinary temperatures; it fumes strongly in air, and is instantly decomposed by water into hydrochloric and boracic acids. It has a sp. gr. of 4.079, and contains 1 equivalent of boron, and

3 equivalents, or 6 volumes of chlorine condensed into the space of 4 volumes; 2 volumes of this chloride unite with 3 volumes of ammonia, and condense to a volatile crystalline saline body.

(394) FLUORIDE OF BORON, ( $\text{BF}_3$ ); *Equivalent*, 68; *Specific Gravity*, 2.312 (Dumas).—With fluorine boron forms a compound analogous to the fluoride of silicon. It is best prepared as follows: 2 parts of fluorspar and 1 of vitrified boracic acid, both in fine powder, are intimately mixed, and intensely ignited in a wrought-iron tube closed at one end; decomposition occurs thus:  $3 \text{CaF} + 4 \text{BO}_3 = 3 (\text{CaO}, \text{BO}_3) + \text{BF}_3$ . Borate of lime remains in the tube, and the fluoride of boron passes over as colourless gas, which may be collected over mercury. It does not support combustion; it has an irritating odour, and fumes densely in the air. It is instantly absorbed by water, which dissolves 700 times its volume of the gas, with rapid rise of temperature, whilst it increases in density to 1.77, and forms a dense, fuming, and corrosive acid liquid, which chars organic matter as powerfully as oil of vitriol. This solution has been called *borofluoric acid*: when heated, a part of the gas escapes, and the specific gravity of the liquid becomes reduced to 1.584; when of this density it distils unchanged, and contains 2 equivalents of water. The reaction, when the gas comes into contact with water is sufficiently simple,  $\text{BF}_3 + 3 \text{HO} = (\text{BO}_3, 3 \text{HF})$ ; the formula of the aqueous solution becomes  $\text{BO}_3, 3 \text{HF}, 2 \text{aq}$ . Borofluoric acid is also easily prepared by saturating hydrofluoric acid with boracic acid, keeping the mixture cool, and then concentrating it in platinum vessels till dense fumes arise.

When largely diluted with water, one-fourth of the boron separates as boracic acid, and another compound is found in solution termed *hydrofluoboric acid*. In composition this body somewhat resembles the silicofluoric acid, though it is not strictly analogous to it. Its formation is readily explained by the following equation, from which it will be seen that hydrofluoboric acid contains the elements of 1 equivalent of hydrofluoric acid and 1 equivalent of fluoride of boron:—



So strong is the tendency to the formation of this compound in dilute solutions, that if boracic acid be added to a solution of fluoride of potassium or of ammonium, for each equivalent of boracic acid present, 3 equivalents of potash or of ammonia are liberated; and fluoboride of the base is formed; for example,



(395) *Nitride of Boron* (BN).—Boron combines with nitrogen to form a white insoluble compound, discovered by Mr. Balmain, which may be easily prepared according to Wöhler's plan (*Q. J. Chem. Soc.* iii. 167):—1 part of anhydrous borax is mixed with 2 parts of sal ammoniac, and heated to full redness in a covered platinum crucible; a white, infusible, porous mass is left, which when boiled with dilute hydrochloric acid and well washed, yields the nitride of boron as a white, light, amorphous powder, which feels like talc when rubbed upon the skin. It may be heated in hydrogen or chlorine without change, and is but very slowly acted upon by concentrated acids or alkaline solutions; but when fused with hydrate of potash it is resolved into ammonia and boracic acid, which latter combines with the potash. In a current of steam it is completely decomposed into borate of ammonia;  $\text{BN} + 4 \text{HO} = \text{H}_4\text{NO}, \text{BO}_3$ .

## CHAPTER IX.

### OTHER COMPOUNDS OF THE NON-METALLIC ELEMENTS.

#### § I. COMPOUNDS OF HYDROGEN AND OXYGEN.

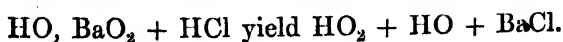
(396) BINOXIDE OF HYDROGEN, ( $\text{HO}_2$ ); *Equivalent*, 17; *Specific Gravity of the Liquid*, 1.453.—Water is not the only compound of oxygen with hydrogen. M. Thénard, in the year 1818, discovered a remarkable substance, which, as it contains 2 equivalents of oxygen in combination with 1 of hydrogen, is termed binoxide of hydrogen. It is a colourless liquid, of syrupy consistence, with an odour somewhat resembling that of chlorine very much diluted; it has never been frozen. It is a very unstable compound; a temperature of about  $70^\circ \text{F}$ . is sufficient to cause the oxygen to begin to escape in small bubbles, and when heated to the temperature of boiling water, the gas is evolved with a rapidity almost amounting to an explosion. The liquid mixes with water in all proportions; and when diluted it is less easily destroyed by elevation of temperature, though ebullition for a few minutes is sufficient to expel the whole of the additional equivalent of oxygen, water alone remaining. This circumstance furnishes an easy method of analysing the binoxide of hydrogen. A given weight of the liquid is placed in a small retort, and diluted with ten or twelve times its bulk of water; the temperature is raised to ebullition, oxygen is given off freely, and the gas is collected over mercury, and measured when cool: the weight of the oxygen can be calculated from its bulk, and deducting

the weight thus obtained from that of the binoxide operated upon, it will be found that for each 8 grains of oxygen expelled, 9 of water remain; consequently, as water contains 1 grain of hydrogen combined with 8 of oxygen, the binoxide of hydrogen will contain 1 grain of hydrogen united with 16 grains of oxygen.

Binoxide of hydrogen bleaches solution of litmus, and many vegetable colours; a drop of it, if placed upon the tongue, blanches it, and destroys sensation for a time; the taste of the liquid is astringent and somewhat metallic. By means of binoxide of hydrogen the black sulphide of lead ( $\text{PbS}$ ) is converted into sulphate of the metal ( $\text{PbO}$ ,  $\text{SO}_3$ ), and many metallic protoxides become oxidized to the maximum.

The binoxide of hydrogen, however, is not only decomposed by substances which possess an affinity for oxygen, but the mere contact of many finely divided metals and metallic oxides, which do not undergo any permanent change, occasions its decomposition; gold, silver, and platinum produce an instantaneous evolution of oxygen gas, which is the more rapid the finer the subdivision of the body by which the decomposition is occasioned. A similar effect is produced by contact with the oxides of these metals, or with the peroxide of manganese or of lead. It is especially to be remarked that the oxides of silver, of gold, and of platinum, not only decompose the binoxide, but they are themselves reduced to the metallic state. These decompositions are all rendered less rapid by the addition of a few drops of sulphuric or hydrochloric acid, but are hastened by the addition of a little free alkali.

Owing to the unstable character of the binoxide of hydrogen, its preparation is attended with great difficulty, although in principle the process is simple. An indirect method is resorted to for procuring it: caustic baryta ( $\text{BaO}$ ), when heated to dull redness in a current of oxygen gas, combines with an additional equivalent of oxygen, and becomes peroxide of barium ( $\text{BaO}_2$ ): when this substance is moistened with water it forms a hydrate ( $\text{BaO}_2 + 6 \text{HO}$ ). The binoxide of hydrogen is obtained from this hydrated compound by decomposing it by means of hydrochloric acid. The hydrated peroxide of barium is reduced to a paste by grinding it in a mortar with water, and is added in small quantities at a time to hydrochloric acid diluted with water, and kept cool by immersing the vessel in ice and water; the peroxide gradually dissolves without effervescence, chloride of barium and binoxide of hydrogen being formed, as is shown in the following equation:—



When the hydrochloric acid is nearly saturated with the peroxide, the chloride of barium is decomposed by the cautious addition of diluted sulphuric acid; an insoluble sulphate of baryta precipitates, hydrochloric acid is set free, and is able to decompose a fresh quantity of peroxide of barium, which must be added with the same precautions as at first. The addition of sulphuric acid produces no change on the binoxide of hydrogen which is present in the solution: it is merely an expedient for getting rid of the baryta and liberating the hydrochloric acid.

The sulphate of baryta is next removed by filtration, and the liquid thus left, is simply a very dilute solution of binoxide of hydrogen with an excess of hydrochloric acid. This acid is again able to decompose a fresh portion of the binoxide of barium. The same series of operations is repeated upon the liquid three or four times in succession, alternately adding binoxide of barium, and removing the barium in the form of sulphate of baryta, until a liquid is obtained which consists of dilute binoxide of hydrogen containing thirty or forty times its bulk of oxygen, and a large quantity of hydrochloric acid. The hydrochloric acid has now to be removed, and this is effected by adding sulphate of silver, until a trace only of hydrochloric acid is left in the liquid. Sulphuric acid is thus substituted for the hydrochloric acid, which is removed in the form of the insoluble chloride of silver, while the binoxide of hydrogen remains unchanged in the liquid.

The sulphuric acid is now got rid of by the careful addition of baryta water, which is at last added drop by drop, so as to remove the whole of the sulphuric acid without introducing any excess of baryta: the liquid is once more filtered, and is now a pure solution of the binoxide of hydrogen in water; finally, it may be transferred to a basin and placed over sulphuric acid in the exhausted receiver of the air pump. The water evaporates much more rapidly than the binoxide of hydrogen, which is thus at length obtained in a concentrated form.

(397) *Teroxide of Hydrogen*, ( $\text{HO}_3?$ ).—The researches of Baumert (Poggendorff, *Annal.* lxxxix. 38) upon the gas disengaged from dilute sulphuric acid, from solution of bichromate of potash, and from various other liquids, during electrolysis, have rendered it probable that a compound of hydrogen with 3 equivalents of oxygen is formed in minute quantity during the operation, and occasions the peculiar smell of ozone which accompanies the oxygen. ✕ Traces only of the compound are formed, so that it is difficult to procure a sufficient quantity of it for analysis, and no means have yet been

devised for separating it from the gas by which it is accompanied. A temperature below redness decomposes it into water and free oxygen.

## § II. COMPOUNDS OF CARBON AND HYDROGEN.

(398) The compounds of carbon with hydrogen are numerous. They are all derived from the decomposition of bodies of organic origin. Many of these bodies exhibit absolute identity in the proportion of the two elements which compose them, although they are endowed with properties perfectly distinct; and from the different densities of these bodies in the gaseous or vaporous condition, it is obvious that the condensation of their particles is different. For example, the following are a few of the many compounds which contain in 100 parts 85.72 of carbon, and 14.28 of hydrogen:—

Olefiant gas	. $C_4H_4$	. specific gravity, 0.978
Oil gas	. . . $C_8H_8$	. " " 1.852
Naphthene	. . $C_{16}H_{16}$	. " " 3.852
Cetylene	. . $C_{32}H_{32}$	. " " 7.846

Such bodies are said to be *polymeric*. At present it will not be necessary to describe more than three compounds of carbon and hydrogen—viz., olefiant gas, marsh gas, and oil gas.

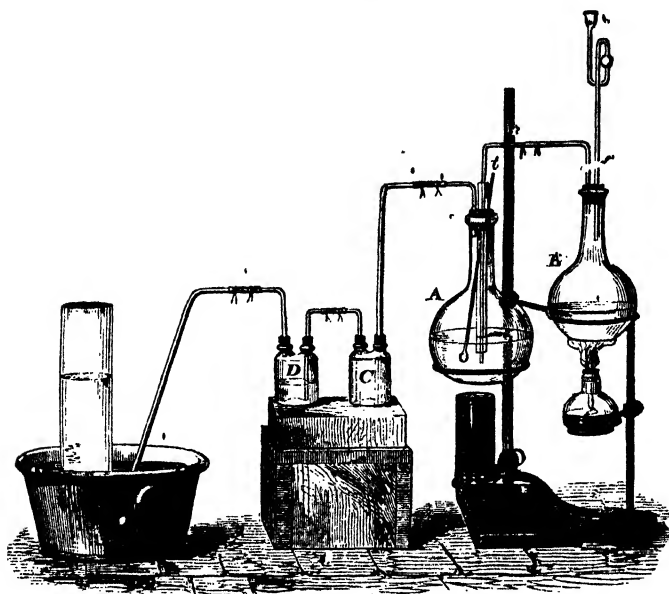
(399) OLEFIANT GAS: *Elayl*, or *Ethylene*, ( $C_4H_4$ ); *Equivalent*, 28; *Specific Gravity*, 0.9784; *Combining Volume*, 4.

*Preparation*.—If 2 measures of concentrated sulphuric acid be mixed with 1 measure of alcohol, in a retort capable of containing at least four times the bulk of the liquid introduced, on distillation a transparent colourless gas is obtained, consisting of carbon and hydrogen. It is accompanied by the vapour of ether, and towards the close of the process by sulphurous acid in large quantity. The *olefiant gas*, as this compound of carbon and hydrogen is termed, at first comes off freely, but by degrees the mixture blackens and becomes thick, and froths up considerably, so that the operation requires careful watching in its latter stages. The gas may be purified by causing it first to pass through an empty bottle, kept cool by immersion in water, in order to condense the vapours of alcohol and ether; it is washed in a solution of potash, to absorb sulphurous acid, and the last traces of ether are removed by allowing it to bubble up through concentrated sulphuric acid, and finally to traverse a tube filled with fragments of pumice moistened with oil of vitriol.



A more elegant method of obtaining the gas was devised by Mitscherlich : it is shown at fig: 274, in which A represents a flask

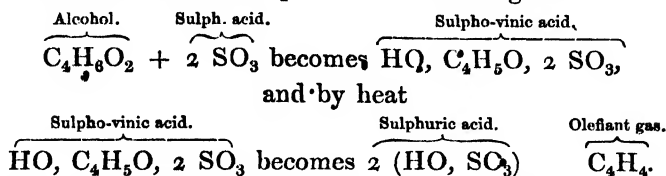
FIG. 274.



containing oil of vitriol, diluted with one-third of its weight of water ; B is a second flask containing alcohol ; C an empty bottle for condensing any alcohol and water which may distil over ; D is a wash-bottle containing solution of potash. The acid in A is brought to the boiling point (about  $325^{\circ}$  F.); the alcohol is also converted into vapour, and made to pass over into the flask, A, in such quantity as just to maintain the boiling point of the acid at from  $325^{\circ}$  to  $330^{\circ}$ ; at this particular temperature, the alcohol, by contact with sulphuric acid, is completely decomposed into olefiant gas and water. Sulphuric acid possesses the remarkable property of producing this decomposition without itself apparently undergoing any change ; the bulk of the sulphuric acid does not alter during the operation, and the same limited amount of sulphuric acid may be employed to convert an indefinite and almost unlimited amount of alcohol into olefiant gas and water.

This circumstance, however, may be thus explained : alcohol enters into combination with sulphuric acid, and forms a peculiar compound acid—the sulpho-vinic acid, which is decomposed by a high temperature ; the sulphuric acid is liberated in an unchanged condition, whilst the alcohol breaks up into water and olefiant gas,

whilst a portion of the water with which the acid was at first diluted distils off, and accompanies the olefiant gas:—



*Properties.*—Olefiant gas is transparent and colourless; it has a faint sweetish odour, and is soluble in about twelve times its bulk of cold water. It was liquefied by Faraday under great pressure, but remained unfrozen at  $-166^\circ$ . Olefiant gas does not support life or combustion, but is itself very inflammable, and burns with a white luminous flame, depositing carbon abundantly upon cold bodies which are introduced into its flame. If a succession of electric sparks be passed through the gas, or if it be transmitted through porcelain tubes heated to bright redness, it is decomposed; half its carbon is deposited, and another compound of carbon with hydrogen (light carburetted hydrogen) is formed, which occupies the same volume as that of the olefiant gas from which it was produced. If the heat to which the gas is subjected be extremely intense, all the carbon is deposited, and for each volume of gas decomposed 2 volumes of hydrogen are liberated.

The composition of olefiant gas may be ascertained by detonation with oxygen; the explosion, however, is very powerful, and requires care, otherwise the eudiometer will be broken. One volume of the gas requires for its complete combustion 3 volumes of oxygen; 2 volumes of carbonic acid remain and represent 2 out of the 3 volumes of oxygen,\* whilst the other volume of oxygen has condensed as steam, and consequently has combined with 2 volumes of hydrogen; 2 volumes of hydrogen and 2 of carbon vapour have therefore condensed in olefiant gas into the space of 1 volume.

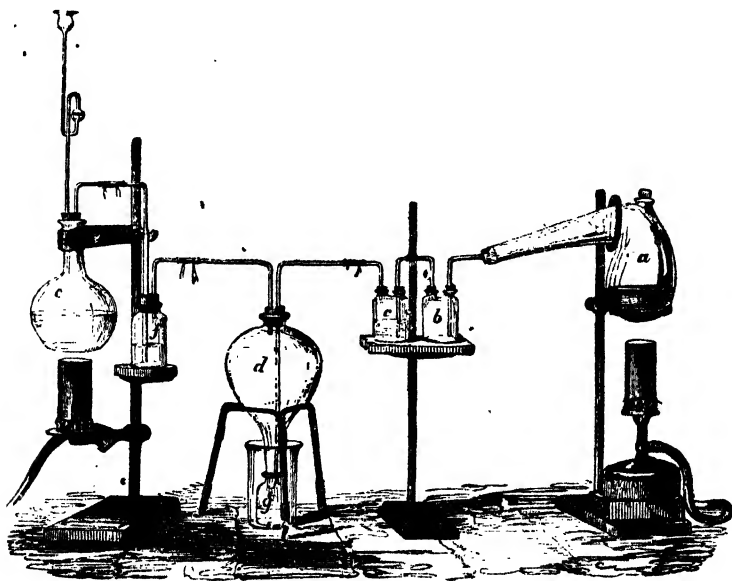
Olefiant gas is slightly soluble in alcohol, oil of turpentine, and the fixed oils. It combines with anhydrous sulphuric acid, forming with it a peculiar compound; hence it is completely absorbed by fuming sulphuric acid; and it also combines with, and is absorbed by, the perchloride of antimony. Olefiant gas, when mixed

\* Carbon has never been volatilized; but it is assumed that when it forms gaseous compounds, 1 equivalent of carbon, like most of the other elements, furnishes 2 volumes of vapour. The specific gravity of this vapour would be 0.4146. Carbonic acid would contain equal volumes of carbon vapour and of oxygen: 2 volumes of carbon vapour and 2 of oxygen condensing so as to form but 2 volumes of carbonic acid when united.

over water with an equal volume of chlorine, condenses to a heavy, sweetish, aromatic liquid: it collects into oily-looking drops, which sink in water: it was owing to this reaction that the name of olefiant (or oil-producing gas) was given to it, and the oily body itself is commonly known as *Dutch liquid*, from the circumstance of its discovery in Holland. If 1 measure of olefiant gas be mixed with 2 measures of chlorine, the mixture may be kindled by a lighted taper, and will burn quietly, depositing the whole of the carbon of the gas in the form of a dense smoke, whilst the hydrogen unites with the chlorine to form hydrochloric acid.

(400) DUTCH LIQUID, ( $C_4H_4Cl_2$ ) or ( $C_4H_3Cl$ ,  $HCl$ ). — This is a compound of considerable interest, as it is the substance from which the chlorides of carbon were originally obtained by Faraday; and the careful study (since made by Regnault) of the stages of the process by which these substances are formed, illustrates in a striking manner the mode in which compounds may be procured by a process of substitution in which the hydrogen of the original body is displaced by chlorine. Dutch liquid is required in considerable quantity for these experiments; it may be obtained by means of an apparatus similar to that represented in fig. 275: *a*

FIG. 275.



is a retort containing the mixture of sulphuric acid and alcohol, which is to furnish the olefiant gas; *b* is an empty bottle to con-

dense the vapours of alcohol and ether; *c* a vessel containing sulphuric acid for absorbing any uncondensed vapour of ether; *d* is a large glass receiver, in which the current of olefiant gas is mingled with a stream of chlorine disengaged from the flask, *e*, and which is washed by passing through the water contained in the bottle, *f*. The olefiant gas is supplied so that it shall always be in slight excess over the chlorine; the operation is best conducted in full diffused daylight. The two gases rapidly combine, and condense in oily drops, which run down the sides of the receiver, *d*, and are collected in the bottle, *g*.

Dr. Limpricht has simplified this apparatus by transmitting the olefiant gas through the mixture of oxide of manganese, common salt, and sulphuric acid, from which the chlorine is generated. The olefiant gas is conveyed into this mixture by means of a bent tube which passes through the tubulure of the retort, and the Dutch liquid as it forms, distils over into a receiver connected with the retort.

The Dutch liquid obtained by either of these processes, when purified by agitation with water, furnishes a liquid which is not miscible with water, but dissolves freely in ether and in alcohol; it has a specific gravity of 1.28 at 32°, boils at 184° F., and emits a vapour the density of which is 3.45. The simplest supposition respecting the composition of this liquid, since it consists of equal volumes of chlorine and of olefiant gas, is that 2 volumes or 1 equivalent of chlorine, is combined with 2 volumes of olefiant gas ( $C_2H_2Cl$ ); whence the equivalent of olefiant gas should be one-half of that which has been given in paragraph (399). The investigations of M. Regnault have, however, rendered it probable that the composition of Dutch liquid is not correctly represented by so simple a formula, and that the equivalent is not ( $C_2H_2Cl$ ), but just double. The usual combining volume of an equivalent of such vapours is four times that of oxygen, and the density of the vapour, as obtained by experiment, coincides almost exactly with that required by the supposition that the formula is ( $C_4H_4Cl_2$ ).

$$Cl_2 = 4 \text{ vol. chlorine,} = 4 \times 2.47 = 9.880$$

$$(C_4H_4) = 4 \text{ vol. olefiant gas} = 4 \times 0.978 = 3.912$$

$$\text{Calculated vapour density} = \left\{ \frac{13.792}{4} = 3.448 \right.$$

The formula for Dutch liquid is commonly written  $C_4H_3Cl + HCl$ .

It was ascertained by Faraday that when Dutch liquid is exposed in a glass vessel with chlorine to the direct rays of the

sun, taking care to renew the chlorine as long as it is absorbed, that the liquid is ultimately converted into the white crystalline and volatile sesquichloride of carbon, whilst a very copious disengagement of hydrochloric acid gas takes place.

M. Regnault has shown that this formation of the sesquichloride of carbon is the result of the interchange of chlorine for hydrogen in the composition of the Dutch liquid; so that sesquichloride of carbon may be regarded as Dutch liquid in which the place of the hydrogen is supplied by chlorine: and he has described a series of compounds intermediate between this liquid and Faraday's sesquichloride of carbon.

For example: if chlorine be transmitted through Dutch liquid the gas is rapidly absorbed, and the liquid acquires a yellow colour, which disappears with copious evolution of hydrochloric acid when it is brought into the sun's rays: by carefully adjusting the addition of chlorine a new liquid was obtained, which boiled at  $239^{\circ}$  F. and had a specific gravity of 1.422. Two equivalents of chlorine had acted upon the Dutch liquid, 1 equivalent had combined with 1 equivalent of hydrogen to form the disengaged hydrochloric acid, while the second equivalent of chlorine took the position of the displaced hydrogen: thus,  $(C_4H_3Cl, HCl) + 2 Cl = (C_4H_2Cl_2, HCl) + HCl$ . This new liquid may be made to absorb a fresh quantity of chlorine, and in the sun's rays it undergoes a change analogous to the preceding; a liquid is formed which boils at  $275^{\circ}$ , and has a density of 1.576;  $(C_4H_2Cl_2, HCl) + 2 Cl = (C_4HCl_3, HCl) + HCl$ . This third liquid, if again acted upon by chlorine under the influence of two more equivalents of this gas, undergoes a further similar decomposition; a still heavier liquid, of specific gravity 1.663, boiling at  $307^{\circ}$  F. is produced, and  $(C_4HCl_3, HCl) + 2 Cl$  become  $(C_4Cl_4, HCl) + HCl$ : and finally, this fourth liquid, when acted upon by an excess of chlorine, loses the remaining equivalent of hydrogen, and becomes the solid sesquichloride of carbon; for  $(C_4Cl_4, HCl) + 2 Cl$  give  $(C_4Cl_5, Cl_2) + HCl$ .

*Chlorinated Compounds derived from Dutch Liquid.*

	Boiling point $^{\circ}$ F.	Specific gravity.		Formula.
		Liquid.	Vapour.	
Dutch liquid . . . . .	184	1.280	3.45	$C_4H_3Cl, HCl$
Monochlorinated ditto . . . . .	239	1.422	4.60	$C_4H_2Cl_2, HCl$
Bichlorinated " . . . . .	275	1.576	5.79	$C_4HCl_3, HCl$
Trichlorinated " . . . . .	307	1.663	7.08	$C_4Cl_4, HCl$
Sesquichloride of carbon . . . . .	356		8.16	$C_4Cl_5$

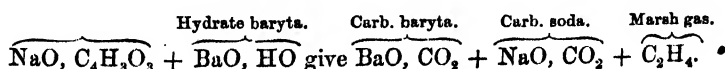
It will be seen that as the quantity of chlorine increases the boiling point rises, and the density both of the liquid and of the vapour increases; in every case one equivalent of the compound yields 4 volumes of vapour.

**LIGHT CARBURETTED HYDROGEN:** *Subcarburetted Hydrogen; Marsh Gas, or Fire Damp, (C<sub>2</sub>H<sub>4</sub>); Equivalent, 16; Specific Gravity, 0.5596; Combining Volume, 4.*

(401) *Preparation.*—This gas is best obtained in a state of purity by a process recommended by Persoz: 10 $\frac{2}{3}$  parts of the hydrate of baryta and 1 $\frac{1}{2}$  of anhydrous acetate of soda, are very intimately mixed, and heated over a charcoal fire in a Florence flask, coated with a luting of fire clay made into a paste with solution of borax. The flask is fitted with a cork and bent tube, and the gas is collected over water in the usual way.\* The hydrate of baryta may be replaced by a mixture of 2 parts of caustic potash and 3 of quick lime. The gas is also easily procured (mingled with nitrogen and carbonic acid), as a result of the decomposition of vegetable matter contained in the mud of stagnant pools; and hence its name of *marsh gas*. In order to collect the gas from this source a bottle may be filled with water, inverted in the pool, and having introduced a funnel into the neck of the bottle, the mud beneath is stirred with a stick; the gas then rises into the bottle in bubbles.

Light carburetted hydrogen is one of the principal constituents of coal gas; it also occurs abundantly in many coal mines, bursting forth unexpectedly from the seams of coal, and blowing out from the fissure for many months together, as though escaping from under high pressure. These natural discharges of the gas the miners term 'blowers.'

*Properties.*—Subcarburetted hydrogen is a colourless, inodorous, and tasteless gas, scarcely soluble in water; not injurious to life if diluted with air. It does not support combustion, but is itself inflammable, and burns with a yellow luminous flame. By passing through it a continued succession of electric sparks, or by sending it through tubes heated to whiteness, it is decomposed; its carbon is deposited, and a volume of hydrogen, double that of the gas employed, is set at liberty. A mixture of this gas with a variable proportion of olefiant gas constitutes the most important ingredient of coal gas. Marsh gas requires twice its volume of oxygen for complete combustion. The 3 volumes of the mixed gases after de-



tonation, are condensed into 1 volume ; they yield 1 volume of carbonic acid and a little water : now carbonic acid contains its own bulk of oxygen ; it therefore represents one of the 2 volumes of oxygen which have disappeared, whilst the other volume of oxygen has united with 2 volumes of hydrogen and formed water. Light carburetted hydrogen must consequently contain its own volume of carbon vapour, and twice its volume of hydrogen condensed into the space of 1 volume.

When mixed with air, an explosive mixture is formed, which takes fire on the approach of a light, and often occasions accidents attended with loss of life to those who are engaged in coal mines.

The fatal results of an explosion of fire-damp in the mine are not, however, limited to the mechanical violence which it occasions to the sufferers. The 'after-damp,' as the miners term it, or vitiated atmosphere that the explosion produces, is often fatal to those employed in other parts of the mine, or to the generous but ignorant and rash survivor who attempts to descend into the pit before it has been properly ventilated, in order to succour his comrades, or to ascertain their fate.

From the composition of fire-damp it is obvious that this gas in exploding renders ten times its bulk of atmospheric air unfit for respiration ; the 2 volumes of oxygen which this air contains producing 1 volume of carbonic acid, and 2 volumes of steam which condense, leaving 8 volumes of nitrogen at liberty.

It was with a view of discovering some means of preventing these fatal results that Sir H. Davy instituted those important researches on flame, which led him to the invention of the *safety lamp*, an instrument which has prevented many serious accidents, and has enabled many coal fields to be worked which otherwise must have been abandoned, on account of the abundant escape of fire-damp from the workings.

(402) *Principle of the Safety Lamp.*—The temperature required for the combustion of different bodies varies greatly ; some take fire at a very low temperature, phosphorus, for instance, with the heat of the body ; sulphur at about  $480^{\circ}$  ; others, as olefiant gas and hydrosulphuric acid, need a red heat. A high temperature is however essential to the existence of flames, and, particularly of flames produced by the combustion of the hydrocarbons. Subcarburetted hydrogen, although an inflammable gas, requires a much higher temperature to ignite it than most other inflammable bodies ; it will not explode when mixed either with less than four times its bulk of atmospheric air, or with more than sixteen times

its volume; the gas in this case burns only in immediate contact with the flame of the lamp, as the large volume of air with which it is mixed prevents the temperature from rising to the point necessary for the general conflagration of the gas; the most powerful explosion is occasioned when the gas is mixed with seven or eight times its bulk of air.

Combustion may often be carried on below the point of inflammation. The smouldering wick of a taper recently blown out is a case in point. Again, if a glowing coil of platinum wire, or a hot slip of platinum, be suspended in a current of coal gas mixed with atmospheric air, the metal will be maintained at a red heat by the rapid combination of the oxygen with the gas, which, however, does not take fire until the platinum becomes heated to whiteness.

Davy found that no explosion could be produced in a mixture of air and fire damp, through a narrow tube, owing to the cooling influence which the tube exerted upon the gas; and the narrower the tube, the shorter was the length required to produce this protective effect. Hemming's safety tube for the oxyhydrogen blowpipe (294) depends for its efficacy upon the cooling influence which the metallic tubes or channels, formed by the interstices between the wires, exert upon the burning jet of gas. The heat of the flame is in this way prevented from passing backwards and causing the explosion of the mixed gases in the reservoir.

If a stout copper wire be introduced into any flame, it will be observed that a dark space immediately surrounds the wire; a second wire cools the flame still further; and a small flame may be completely extinguished by the cooling effect produced by bringing down a coil of wire upon it; but if the same coil be previously heated to redness, and, whilst still hot, be placed over the flame, the latter will continue to burn.

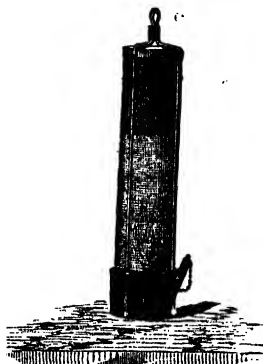
By using wire gauze we may easily cut off the upper part of a flame, the unburned gases being reduced in temperature below the point of inflammation; if a piece of gauze with large meshes be employed, it will cut off the flame so long as it remains cold, but the flame will traverse the network as soon as the wire becomes red hot: with finer meshes (about 400 to the square inch) the conducting power of the metal is sufficient to cool the flame below the point of ignition, even though the wire itself be red hot. In a similar manner the gas above the gauze may be kindled, and the flame will not pass through to the gas below. Advantage is taken of this circumstance in the laboratory to obtain a smokeless flame by the use of ordinary coal gas:—A metal chimney, five or six inches long, open below, and furnished at top with a cap of wire



gauze is placed over any convenient form of burner; the air enters at the bottom and mixes with the gas, which burns above the wire gauze with a blue flame, which emits scarcely any light and deposits no smoke upon cold objects, provided that the supply of gas be duly proportioned to that of the air which mixes with it.

These principles were beautifully applied by Sir H. Davy in

FIG. 276.



the construction of his miner's lamp, which is merely an oil lamp, fig. 276, inclosed within a cylinder of wire gauze, provided with a double top, and with a crooked wire, *w*, which passes up tightly through a tube traversing the body of the lamp for the purpose of trimming the wick without the necessity for removing the wire covering. When such a lamp is introduced into an explosive atmosphere of fire damp, the flame is seen gradually to enlarge as the proportion of carburetted hydrogen increases, until at length it

fills the entire gauze cylinder: when the gas is in sufficient excess the lamp is entirely extinguished; if it be withdrawn from the explosive mixture while the cylinder appears full of flame, it generally rekindles the wick, and the lamp continues to burn in air as usual. Whenever this pale, enlarged flame is seen, the miner must withdraw; for though no explosion can occur while the gauze is sound, yet at that high temperature the metal becomes rapidly oxidized, and might easily break into holes; a single aperture of sufficient size would then determine the fatal explosion.

The wire gauze used in the construction of these lamps contains from 700 to 800 meshes in the square inch. In a strong current of air the heated gas may be blown through the apertures of the gauze before its temperature is sufficiently reduced to prevent the explosion, but such an occurrence may be easily guarded against by the use of a screen.

(403) *Nature of Flame.* — It is necessary to the production of flame, that the combustible be of such a nature as to be convertible into vapour before it undergoes combustion, otherwise no flame results. Well burned charcoal or diamond burns with a steady glow, unattended with flame, as does also iron wire. None of these substances are susceptible of volatilization at the temperature attending their combustion. Sulphur, phosphorus, zinc, and the various

combustible gases, burn with flame as they pass into the aeriform state before combination.

Flame is, in fact, produced whenever, by a sufficiently elevated temperature, a continuous supply of combustible vapour, or gas, is made to combine with atmospheric oxygen, or with some supporter of combustion, as they come into contact. In all ordinary cases, therefore, flame is a luminous envelope which forms a limiting surface between the unburned combustible within and the supporter of combustion without.

This hollow structure of flame may be easily proved by experiment. If a wooden match be held for a few seconds across the middle of the flame of a spirit lamp with a large wick, the match will become charred at the edges of the flame, but the intermediate portion will remain uninjured. If a fragment of phosphorus be placed in a small deflagrating spoon, ignited, and then introduced into the middle of the flame, it will be extinguished, but it will burn with its former energy the moment that the spoon is withdrawn from the flame. The tapering form which flames assume, is due to the ascending current produced in the atmosphere by the heat attendant on the combustion. Within the burning portion of flame is an atmosphere of unburned combustible matter: by inserting into a flame, such as that of a wax candle, just above the wick, the lower extremity of a glass tube, open at both ends, about one-third of an inch in diameter, and five or six inches long, the gases in the interior may be drawn off, and may be ignited at the upper aperture of the tube.

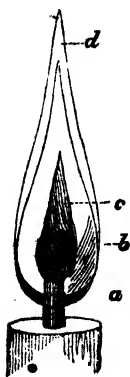
It is important to remark that the light and the heat emitted by flames are by no means proportional to each other. The heat is due solely to the energy of the chemical action; and when a pure gaseous matter, without solid particles, composes both the burning body and the product of the combustion, little or no light is emitted: the flame of a jet of hydrogen is barely visible in clear daylight; and that of the oxyhydrogen jet itself, although one of the most intense sources of heat at our command, is scarcely more luminous than the flame of hydrogen. For the same reason the light of sulphur burning in oxygen is feeble, notwithstanding the intense energy with which they combine: both the vapour of sulphur and sulphurous acid are gaseous bodies. Phosphorus and chlorine, though they unite so energetically as to take fire at ordinary temperatures by mere contact, yet emit but little light during their combustion; the chlorides of phosphorus, as well as phosphorus itself, being very volatile bodies.

In all luminous flames the light is emitted from solid particles highly ignited. The light from bodies feebly ignited is red; as the temperature rises the light becomes yellow, then white, and when the heat is very intense, the more refrangible rays of the spectrum predominate, so that it has a shade of blue or violet.

By introducing a solid object into a non-luminous flame, a platinum wire, for example, into the oxyhydrogen jet, or, better still, a body which, like lime, does not melt at that temperature, the light becomes so intense that the eye can scarcely support it. Such bodies, however, since they do not contribute to the chemical changes occurring in the flame, necessarily reduce its heat owing to their conducting power. It is immaterial whether the bodies so introduced be combustible, or have already undergone perfect combustion:—the flame of hydrogen may be rendered luminous either by blowing a little powdered charcoal through it, or by allowing finely powdered magnesia, oxide of zinc, or the white fumes of phosphoric acid produced by the combustion of phosphorus, to traverse it. Indeed no better illustration of this point can be given than is afforded by contrasting the painfully intense light produced by the combustion of phosphorus in oxygen, where the solid non-volatile phosphoric acid is produced, with the feeble light emitted by the same body as it burns in chlorine.

The flames used for illuminating purposes are all produced by the combustion of compounds of carbon and hydrogen. All of them, notwithstanding the perfect transparency of the gas before combustion, contain solid particles of carbon during the act of combustion. The separation of carbon during the process of combustion is seen by the simple expedient of introducing a cold body, such as a plate of metal, or a piece of glass, into a luminous flame; it speedily becomes blackened from the deposition of carbon.

FIG 277.



The flame of a candle is sustained by the decomposition of the melted wax or tallow absorbed by the wick, and its conversion into gaseous hydrocarbons by the heat of the combustion. At the lower part of the flame, *a*, fig. 277, these hydrocarbons are immediately mingled with atmospheric air, no separation of carbon occurs here, and they burn with a pale blue light. The greater portion of the combustible gases and vapours, however, are still unburned; they rise above the wick, forming the central dark part, *b*, of the flame: here they are subjected

to a high temperature from the combustion of the blue portion already mentioned; the heat now causes the separation of the carbon in the solid form, which becomes intensely ignited in the burning gas, emitting light in the part marked *c*; and this carbon itself, in a properly adjusted flame, gradually burns away without residue or smoke, as it comes to the surface, *d*, and meets with oxygen. In order to produce the maximum amount of light, the point which requires the greatest attention is the due adjustment of the supply of air; if too much be given, the gas burns with a blue, feebly luminous flame; an effect which may be seen by blowing upon a common gas flame, or by watching the effects of the wind upon the exposed gaslights at night: the lengthening of the chimney of a lamp produces a similar effect. In these cases the gas becomes immediately mixed with the oxygen of the air, and it is completely burned before it has been exposed to an elevated temperature for a time sufficiently long to allow of the separation of carbon. The supply of air, however, must not be too much limited; otherwise, as may be seen by closing the central tube for the admission of air to an argand burner, the light becomes red from the reduction of temperature, the carbon passes off unburned, and the oxygen being insufficient to complete the combustion, the flame becomes smoky. The light of a flame is increased by any contrivance which, without deranging the order of the combustion, concentrates it into a smaller space, so as to raise the temperature of the deposited carbon to the maximum. It is in this way that an argand burner produces a far greater amount of light with a given consumption of gas, than if the same quantity of gas were burned in separate jets.

(404) *Theory of the Blowpipe.*—The temperature of a flame may be very materially increased by augmenting the activity of the combustion, and concentrating its effect by diminishing the extent of surface over which it would otherwise take place. It is upon this principle that all blowpipes act: a jet of air or of oxygen is thrown into the interior of a flame; the combustion is thus rendered more rapid, it is limited to a much smaller space, and is entirely changed in character.

The mouth blowpipe is one of the most valuable and portable instruments of research which the chemist possesses: he is enabled by its means, in a few minutes to arrive with certainty and economy at results which without its aid would require much expenditure both of fuel and of time; and it often affords information which could be obtained in no other way.

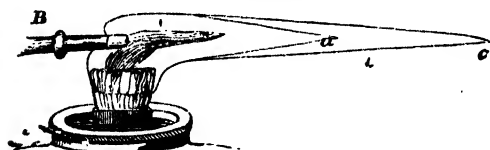
The mouth blowpipe has been constructed in a great variety of forms, but it consists essentially of a bent tube, terminating in a fine uniform jet, with a chamber for the condensation of moisture from the breath. Dr. Black's blowpipe is a very convenient form of the instrument; it is shown at fig. 278.

FIG. 278.



It consists of a conical tube of tin plate, about eight inches long, open at the narrow end, *a*, which is rounded off so as to adapt itself to the lips, and closed at its lower end, from the side of which projects a brass tube about  $\frac{1}{4}$  inch in length, upon which is fitted a small brass jet, *b*. This jet is inserted to a short depth into the flame of a candle, about an eighth of an inch above the wick; when a current of air from the blowpipe is directed horizontally along the surface of the wick, the flame loses its luminosity, and is projected laterally in the form of a beautiful pointed cone, in which three parts are distinctly discernible. See fig. 279.

FIG. 279.



In the centre is a well defined blue cone; outside that is the brilliant part of the flame, terminating at *a*, and exterior to that, is a pale yellow flame, *c*.

The different parts of this flame possess very different properties. The blue cone is formed by the admixture of air with the combustible gases rising from the wick, and it corresponds to the blue portion, *a*, of an ordinary flame, fig. 277. In this part of the flame combustion is complete, and the oxygen introduced by the jet is in excess; the points where the excess of oxygen is absorbed by combination with fresh combustible rising from other parts of the wick, are clearly defined by the surface which seems to limit the blue cone. In front of this blue cone is the luminous portion, containing unburned combustible gases at a high temperature, which of course have a powerful tendency to combine with oxygen. If a fragment of some metallic oxide, such as oxide of copper, sufficiently minute to be completely enveloped by the luminous, portion be introduced into this part of the flame, the oxide will be deprived of oxygen, in consequence of the superior affinity of the hot gases for this element, and the oxide will be reduced to the metallic state: hence this portion is termed the *reducing*

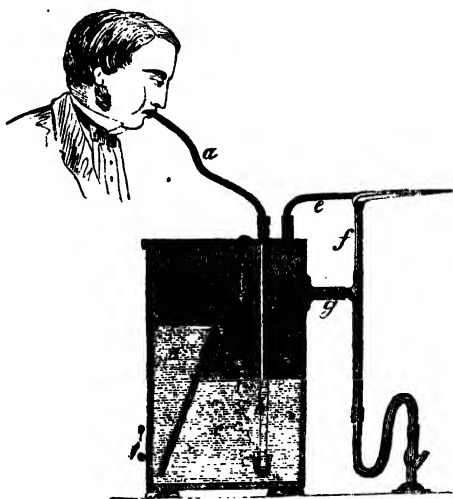
*flame* of the blowpipe. At the apex, *c*, of the flame, the effects are reversed. Here atmospheric oxygen at a high temperature, is mechanically carried forward along with the completely formed products of combustion, and a fragment of any metal, such as lead, copper, or tin, if placed at this point will quickly become coated with oxide; and hence this spot is termed the *oxidating flame* of the blowpipe. A good illustration of the opposite actions of these contiguous portions of the flame is afforded by the effects which they, respectively produce on a piece of flint glass tubing. The silicate oxide contained in the glass is partially decomposed in the reducing flame, and the glass at this point becomes black and opaque from the reduction of the oxide of lead to the metallic state, but by placing the blackened part for a few seconds in the oxidating flame, oxygen is again absorbed by the metal, and the transparency of the glass is restored.

The art of maintaining a continual blast by the mouth blowpipe is not easily described, but it can be acquired by practice without much difficulty.

Different forms of the blowpipe have been proposed, according to the purposes for which it is destined. The glass-worker usually requires a large supply of air to be maintained uninterruptedly for long periods, and he commonly employs a pair of double bellows, worked by the foot.

A very convenient and portable blowpipe for glass working is made as follows: a rectangular box of zinc, fig. 280, about fourteen inches high, and six wide, is divided into two chambers, *c* and *d*, by a diaphragm which passes obliquely nearly to the bottom of the box; these chambers, communicate with each other below; one of them, *d*, is open above, and is covered with a loose lid; the other chamber, *c*, is closed at the top: a blowpipe jet, *e*, passes just through the covering of this chamber, which is further supplied with a longer pipe, *a b*, passing down to within a short dis-

FIG. 280.



tance of the bottom, covered with a flap of silk to prevent the return of the water when the operator suddenly ceases to blow through *a*. If the box be now partially filled with water, the pressure of the column of liquid will expel the air through the jet, *e*, in any desired direction. By blowing down the long pipe, the operator can renew the supply of air as often as may be necessary; it bubbles up into the closed chamber, *c*, driving the water back into the open one, when the column of liquid, by its pressure, renews the blast as before. The gasburner, *f*, can be raised or lowered as may be necessary, and by means of a sliding joint, *g*, can be made to approach towards or recede from the jet, *e*, as may be required.

In the oxyhydrogen blowpipe, owing to the complete intermixture of the two gases, the flame is solid, and therefore of small dimensions.

(405) OIL GAS, ( $C_8H_8$ ); *Equivalent*, 56; *Specific Gravity*, 1·854; *Combining Volume*, 4.—This compound was discovered by Mr. Faraday to be one of the constituents of the gases obtained by the destructive distillation of oil. It condenses at  $0^\circ$  F. to a colourless liquid, of sp. gr. 0·627. at  $54^\circ$ : it is almost insoluble in water, but is taken up freely by alcohol, and still more abundantly by oil of vitriol. Oil gas is colourless, and burns with a white, powerfully luminous flame. It contains the same proportions of carbon and of hydrogen as olefiant gas, but the two elements are condensed in oil gas into half the bulk which they occupy in olefiant gas. 1 volume of this gas requires six times its bulk of oxygen for its complete combustion; water and carbonic acid being the products.

### § III. COMPOUNDS OF CARBON WITH OXYGEN.

Besides carbonic oxide and carbonic acid, carbon forms several other oxides possessed of acid characters: viz.,

Oxalic acid . . . . .	HO, $C_2O_3$
Rhodizonic acid . . . . .	3 HO, $C_7O_7$
Croconic acid . . . . .	HO, $C_6O_4$
Mellitic acid . . . . .	HO, $C_4O_3$

(406) OXALIC ACID, ( $HO, C_2O_3, 2 aq$ ); *Equivalent*, 36 + 27.—This important and powerful acid belongs more properly to the division of organic chemistry, as it is always obtained from sugar, starch, or some other substance of organic origin, and is one of the products of the oxidation of these substances; it is moreover a frequent constituent of the juices of plants. Oxalic acid is abun-

dant in the leaves of the wood sorrel (*Oxalis acetosella*), to which it communicates their powerfully acid taste, and in which it occurs in combination with potash as binoxalate of potash. It is found also in the *Rumex acetosa* and in the leaf-stalks of the common rhubarb. Many lichens owe their solidity to the presence of oxalate of lime, and have even been employed as a source of the acid.

**Preparation.**—Oxalic acid is prepared artificially upon a large scale by the oxidation of sugar or of starch by nitric acid. Berzelius recommends Schlesinger's mode of preparing it, as yielding it in the purest condition and in the largest quantity: 1 part of dry loaf sugar is dissolved in  $8\frac{1}{4}$  parts of nitric acid, of specific gravity 1.38, and heated in a flask until all effervescence has ceased; a copious evolution of carbonic acid and of nitric oxide attends the reaction. The solution is then evaporated by a water bath to one-sixth of its bulk, and the acid crystallizes on cooling. The mother-liquor may be further concentrated by evaporation: the oxalic acid is purified by recrystallization, and amounts to more than half the weight of the sugar employed.

**Properties.**—Oxalic acid as thus obtained crystallizes in transparent four-sided prisms, which are represented by the formula  $(HO, C_2O_3, 2 aq)$ . This acid requires about 9 parts of cold water for solution, but it dissolves much more freely in boiling water; it is also soluble in alcohol. The crystals when heated to  $212^\circ$  become opaque, and lose 28.5 per cent. of water. The residue then consists of  $(HO, C_2O_3)$ , but the remaining equivalent of water cannot be expelled by the mere action of heat; it can only be displaced by some metallic oxide. If the dried crystals be placed in a retort and heated by means of an oil bath to between  $300^\circ$  and  $320^\circ$ , they slowly sublime and condense in white needles; but if heated above  $320^\circ$  the acid is decomposed. When the crystallized oxalic acid  $(HO, C_2O_3, 2 aq)$  is heated quickly without previous desiccation, it melts in its water of crystallization, and at  $311^\circ$  is resolved, with apparent ebullition, into a mixture of carbonic acid, carbonic oxide, water, and formic acid  $(HO, C_2HO_3)$ : the latter is produced by the reaction of the elements of water upon those of oxalic acid.

The solution of oxalic acid has an intensely sour taste; if swallowed, the acid acts as a powerful poison, occasioning death in a very few hours. The best antidote in such a case is the administration of chalk or of magnesia suspended in water.

It is a general rule that when an elementary body forms two or more acids with oxygen, the acid which contains the largest amount



of oxygen is the most energetic in its action. Thus the sulphuric acid is more powerful than the sulphurous:—chloric acid is stronger than the hypochlorous acid; and the perchloric is stronger than either. It is, however, otherwise in the case of oxalic acid. Although oxalic acid contains a smaller proportion of oxygen than carbonic acid, its affinity for bases is much more energetic, and it decomposes all the carbonates with effervescence. The cause of this remarkable exception to the general rule has not hitherto been explained. Berzelius suggests that the carbon in oxalic acid may be in a different allotropic condition to that which exists in carbonic acid. The equivalent of carbon in oxalic acid might therefore be 12, or the double of what it is in carbonic acid; and oxalic acid might thus be a tetroxide of a particular form of carbon,  $\text{CO}_3$ .

On the other hand, the facility with which oxalic acid, under the influence of sulphuric acid (303) is decomposed into carbonic acid and carbonic oxide, renders such a hypothesis very doubtful. Some chemists have been disposed to regard the oxalic acid rather as an oxide of carbonic oxide,  $2(\text{CO})\text{O}$ , than as a true oxide of carbon. Such speculations, however, are valuable rather on account of the experiments and researches which they suggest, than from any inherent probability which they possess.

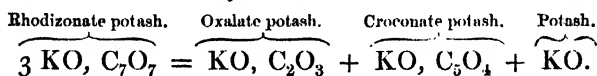
*Oxalates.*—Oxalic acid forms a large number of insoluble salts. The insolubility of oxalate of lime in water has led to the employment of oxalic acid as a reagent for indicating the existence of lime in solution, and for determining its amount. On adding a neutral oxalate to a neutral or alkaline solution of any salt of lime, the oxalate of lime falls as a white precipitate ( $\text{CaO}$ ,  $\text{C}_2\text{O}_3$ , 2 aq) which is insoluble in acetic acid. The oxalates of baryta, strontia, lead, and silver, are also insoluble in water, but all these compounds dissolve readily in dilute nitric acid. The oxalate of copper is a pale blue insoluble powder; and the oxalates of zinc and of manganese are scarcely more soluble. The oxalate of silver is a white salt, which, if heated on platinum foil, is suddenly reduced to the metallic state, and is dispersed with a slight explosion, owing to the sudden liberation of carbonic acid;  $\text{AgO}, \text{C}_2\text{O}_3 = \text{Ag} + 2\text{CO}_2$ . The oxalates of the alkalis and of the alkaline earths are converted by a dull red heat into carbonates of these bases; the carbonic oxide burning off with a pale blue flame, whilst the salt does not exhibit any appearance of charring. The oxalates of many of the metals which have but small affinity for oxygen, are reduced to the metallic state if heated to redness in a closed vessel, so as to exclude atmospheric oxygen; 2 equivalents of carbonic acid gas being expelled,

whilst the pure metal is left behind. This reducing action occurs in the case of gold, when a solution of a salt of this metal is simply boiled with an oxalate; the gold is precipitated, either in flakes or in the form of a very finely divided, powder.

With the alkalis, oxalic acid forms three classes of salts, one of which contains 1 equivalent of base to 1 equivalent of acid, of which the oxalate of ammonia ( $\text{H}_4\text{NO}$ ,  $\text{C}_2\text{O}_3 + \text{aq}$ ) is an example. The second class contains two equivalents of acid to one of a fixed base. ~~Bisoxalate~~ of potash, or the salt of sorrel ( $\text{KO}$ ,  $\text{HO}$ ,  $2 \text{C}_2\text{O}_3 + 2 \text{aq}$ ) is an instance of this description; whilst the third class, which is exemplified by quadroxalate of potash ( $\text{KO}$ ,  $3 \text{HO}$ ,  $4 \text{C}_2\text{O}_3 + 4 \text{aq}$ ) contains the unusual proportion of 4 equivalents of acid to 1 of a fixed base. It is very probable that oxalic acid belongs to the class of acids termed dibasic (460).

(407) *Rhodizonic, Croconic, and Mellitic Acids*.—Three other acids containing carbon and oxygen are known under these names, but they are of slight importance.

*Rhodizonic Acid*, ( $3 \text{HO}$ ,  $\text{C}_7\text{O}_7$ ) is an acid which forms salts of a beautiful red or scarlet colour, whence it derives its name. It is obtained by the action of a moist atmosphere on the dark olive green compound which potassium yields when gently heated in carbonic oxide gas, and which is largely formed during the preparation of potassium. If the aqueous solution of rhodizonate of potash be boiled, it is decomposed into oxalate of potash, and the salt of a new acid, which from the yellow colour of its compounds is termed *Croconic acid*, whilst potash is set at liberty:



Croconic acid is obtained by decomposing croconate of potash by silicofluoric acid. It forms yellow crystals soluble both in water and in alcohol. Croconic acid and the soluble croconates form yellow sparingly soluble crystalline plates when mixed with salts of baryta or of lead.

*Mellitic Acid* ( $\text{HO}$ ,  $\text{C}_6\text{O}_6$ ) has hitherto been found only in a rare mineral, the mellitate of alumina, which is now and then met with in lignite, and occurs crystallized in yellow transparent octohedra. Mellitic acid is extracted from mellitate of alumina by boiling the powdered mineral with carbonate of ammonia. Mellitate of ammonia is obtained in solution: by the addition of acetate of lead to the liquid, the mellitate of lead is precipitated, which, when washed, is suspended in water and decomposed by a

current of sulphuretted hydrogen. Sulphide of lead is formed, and is separated by filtration from the solution which contains the liberated mellitic acid: by evaporation the acid is left in a state of purity. This acid is soluble in water and in alcohol, and it crystallizes in groups of needles by the spontaneous evaporation of the alcoholic solution. Its solution reddens litmus strongly, and has a strong sour taste. Mellitic acid is unchanged by boiling nitric or sulphuric acid. The acid is decomposed by heat, into a volatile crystalline sublimate, and into carbon. With the salts ~~of lead the~~ mellitates give a voluminous white precipitate, which gradually shrinks in bulk and becomes crystalline.

#### § IV. COMPOUNDS OF CARBON WITH NITROGEN.

CYANOGEN, ( $\text{NC}_2$ , or Cy); *Equivalent*, 26; *Specific Gravity*, 1.8064; *Combining Volume*, 2.

(408) Cyanogen, or bicarbide of nitrogen, is one of the most interesting compounds of carbon, and its discovery by Gay Lussac, in 1814, formed an epoch in the history of chemical science. This substance was the first compound body which was distinctly proved to enter into combination with elementary substances in a manner similar to that in which they combine with each other. New views of chemical composition were thus originated, which have since acquired an extensive development, and have exercised a most material influence upon the theory of organic compounds in general. The name of cyanogen (or blue producer), is derived from the circumstance that this body forms an essential ingredient in Prussian blue. It consists of 2 equivalents of carbon and 1 of nitrogen, but no direct union of these elements can be effected. If a mixture of charcoal and of carbonate of potash be heated to redness in a porcelain tube, and nitrogen be passed over it, the potash is reduced to potassium, carbonic oxide escapes abundantly, and cyanogen ( $\text{NC}_2$ ) is formed, and unites with the potassium, yielding cyanide of potassium:  $\text{KO}, \text{CO}_2 + \text{C}_4 + \text{N} = \text{K}, \text{NC}_2 + 3 \text{CO}$ .

The compounds of cyanogen are, however, almost always obtained from the double cyanide of potassium and iron, a salt which crystallizes in transparent yellow tables, and is commonly known by the name of prussiate of potash, or ferrocyanide of potassium. This salt is prepared by heating, in a covered iron pot, about 5 parts of refuse animal matter, such as the parings of hoofs, hides, horns, &c., with 2 parts of pearlash and iron filings; the nitrogen

and carbon of the animal matters react upon each other at a high temperature, and combine with a portion of reduced potassium and with iron. On digesting the mass, when cold, with water, the ferrocyanide of potassium ( $K_2, FeCy_3 + 3, aq$ ) is formed, and is deposited from the solution in large four-sided tables, which contain 3 equivalents of water. When 10 parts of this salt are distilled with 7 parts of oil of vitriol diluted with five or six times its weight of water, hydrocyanic acid ( $HCy$ ) is formed; \* this, if saturated with red oxide of mercury, furnishes, on evaporation, a crystallizable compound, the cyanide of mercury ( $HgCy$ ). If this be thoroughly dried, and heated in a retort, it is decomposed into mercury, which sublimes, and cyanogen, which passes off as a permanent gas.

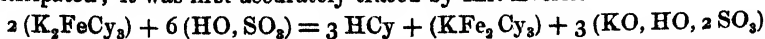
Cyanogen is a transparent, colourless gas, of a peculiar penetrating odour: it is poisonous if respired. It burns with a beautiful purple flame. Cyanogen dissolves in one-fourth of its bulk of water, and still more freely in alcohol; hence it must be collected over mercury. In porcelain or glass vessels it supports a high temperature without decomposition, but if heated in iron tubes, charcoal is deposited, and a volume of nitrogen, equal to that of the cyanogen used, remains.

The composition of cyanogen may be determined by detonation in the eudiometer with oxygen; the combination is attended with a powerful explosion. Two volumes of cyanogen with 4 volumes of oxygen yield 4 volumes of carbonic acid and 2 volumes of nitrogen; 4 volumes of carbon vapour and 2 volumes of nitrogen must therefore be condensed in it into 2 volumes.

Cyanogen is readily reduced to the liquid state by a pressure of its own vapour equal to about four atmospheres. It forms a colourless, limpid liquid, lighter than water, which, on the removal of the pressure, rapidly but quietly resumes the gaseous state. It freezes at  $-30^\circ$  F., and forms a transparent crystalline solid, which is nearly of the same density as the liquid.

Fig. 281 shows an easy method of liquefying cyanogen: a tube of hard glass is bent into the form, *a, b, c*. Into the limb, *a*, well dried cyanide of mercury is introduced; heat is applied to the cyanide of mercury at *a*; the bend, *b*, is placed in a basin con-

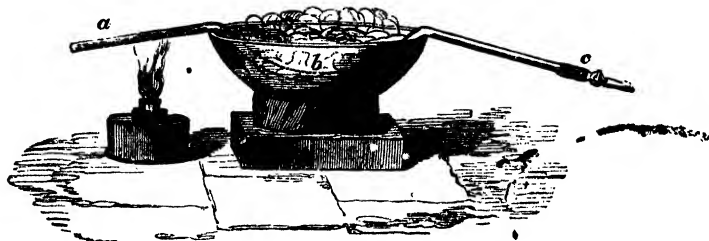
\* The reaction in this case is rather less simple than might have been anticipated; it was first accurately traced by Mr. Everitt:



Half the cyanogen only is expelled as hydrocyanic acid, the other half remaining behind in the form of a white, insoluble, double cyanide of iron and potassium ( $KFe_2Cy_3$ ).

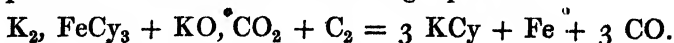
taining a freezing mixture of ice and salt; as soon as the gas begins to escape, the stopcock at *c* is closed, and liquid cyanogen condenses in the bend, *b*.

FIG. 281.



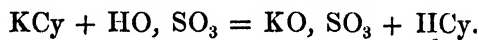
If potassium be heated in cyanogen it burns and combines with it, without occasioning the decomposition of the gas, forming a saline body analogous to common salt. This experiment shows the existence of the remarkable property possessed by cyanogen of combining with metals and other bodies like an element. This peculiarity in the mode of combination of cyanogen, which has given rise to the theory of compound radicles now so extensively applied in organic chemistry, will be better traced by examining a few of the numerous compounds which cyanogen forms with the elementary bodies.

(409) HYDROCYANIC ACID: *Prussic Acid*, (HCy); *Equivalent*, 27; *Specific Gravity of Vapour*, 0.9476; *Combining Volume*, 4.—Cyanogen forms with hydrogen a highly important compound, though the two bodies cannot be made to unite directly with each other. It may be prepared by decomposing any of the cyanides by a strong acid, and subjecting them to distillation. The most economical process is that of Wöhler; he prepares a crude cyanide of potassium by fusing 8 parts of the yellow ferrocyanide of potassium with 3 of carbonate of potash and 1 part of charcoal. In this reaction the potash of the carbonate is deprived of oxygen by the charcoal, and the potassium takes the place of the iron in the ferrocyanide; 3 equivalents of cyanide of potassium being formed; the carbonic acid of the carbonate of potash is also reduced to the state of carbonic oxide by the excess of charcoal which is employed. This decomposition is shown in the following equation:—



The fused mass is treated with six times its weight of water, in a well closed vessel; the clear liquid is decanted from the iron which it is the object of this operation to separate, and is poured into a

retort: sulphuric acid, diluted with an equal weight of water, is gradually added in the proportion of 1 part of oil of vitriol to 2 parts of the cyanide. At first the distillation proceeds spontaneously from the heat developed by the admixture of the sulphuric acid with the water. In order to condense the acid, the products are made to pass through a long U-shaped tube, immersed in cold water, and filled with chloride of calcium, with the exception of the first fourth of the tube, which contains fragments of the crude cyanide of potassium; to the bent tube is attached a second delivering tube, which passes to the bottom of a bottle cooled with ice and salt. The chloride of calcium in the syphon tube retains the moisture, and the cyanide of potassium absorbs any sulphuric acid that might chance to pass over, whilst the hydrocyanic acid collects in an anhydrous state in the cooled receiver. The reaction of sulphuric acid upon cyanide of potassium is very simple, being exactly analogous to its action upon chloride of sodium:



Anhydrous hydrocyanic acid is a colourless, transparent, and very volatile liquid, of a specific gravity of 0.7058 at 45°; it boils at 80°, and freezes at 5°; so rapidly does it evaporate, that if a drop be allowed to fall upon a glass plate, part of the acid becomes frozen by the cold produced by its own evaporation. Its vapour has an odour of peach blossoms, causing a peculiar sense of oppression, and of constriction in the fauces. Owing to its intensely poisonous character, the greatest care is requisite in conducting experiments upon this substance; the apparatus should always be arranged so that the vapours are carried away from the operator by a brisk current of air.

Hydrocyanic acid is very inflammable, and in the gaseous state has a sp. gr. 0.9476. Like the hydrogen acids of chlorine, and the other halogens, it is composed of 2 volumes of hydrogen and 2 of cyanogen united without condensation. If 5 volumes of oxygen be mingled with 4 volumes of this vapour, a mixture is obtained which detonates powerfully on transmitting the electric spark through it; 4 volumes of carbonic acid and 2 volumes of nitrogen remain, and 2 volumes of steam condense. The composition of hydrocyanic acid may be calculated from the result of this experiment.

The acid properties of this compound are but feeble; it reddens litmus slightly, dissolves red oxide of mercury freely, and precipitates nitrate of silver in white flocculi (AgCy). Cyanide of

potassium always has an alkaline reaction: its solution emits the odour of the acid. Pure hydrocyanic acid may be kept unchanged if excluded from light; but in diffused light it becomes decomposed, and a brown matter forms, consisting chiefly of paracyanogen. Pelouze has pointed out a remarkable decomposition which furnishes dilute hydrocyanic acid almost in a state of purity. Crystallized formiate of ammonia contains the elements of 1 equivalent of hydrocyanic acid and 4 equivalents of water. If this salt be placed in a retort and heated, it melts at  $248^{\circ}$ , loses a little ammonia at  $284^{\circ}$ , and between  $356^{\circ}$  and  $392^{\circ}$  F. distils over, and is wholly converted into hydrocyanic acid and water;  $\text{H}_4\text{NO}, \text{C}_2\text{HO}_3 = \text{HNC}_2 + 4 \text{HO}$ .

Hydrocyanic acid is obtained by distillation from the kernels of the bitter almond, and from those of many varieties of stone fruit, as well as from the leaves of the laurel, the peach, and some other shrubs: it is also present in the juice of the tapioca plant (*Jatropha Manihot*), and is found under various circumstances during the oxidation and formation of some kinds of nitrogenized substances.

Hydrocyanic acid is now frequently employed in medicine; and on account of its energetic action, it is highly important to be able to insure its preparation of an uniform strength. This is easily attained by the process of the London Pharmacopœia, which directs  $48\frac{1}{2}$  grains of cyanide of silver to be suspended in an ounce of water, and to be decomposed by  $39\frac{1}{2}$  grains of hydrochloric acid, decanting the clear liquid from the chloride of silver; this acid contains two per cent. of the anhydrous acid. The dilute acid is less prone to decomposition, especially if a little free sulphuric acid be present: but it should always be excluded from the light.

(410) *Cyanides*.—The cyanides of the alkaline metals are freely soluble in water. A large number of the cyanides of the heavier metals are insoluble in water, but most of them are decomposed with evolution of hydrocyanic acid when boiled with hydrochloric acid; those of silver and mercury, when heated to redness, yield cyanogen gas.

The presence of the soluble cyanides, or of hydrocyanic acid in solution, may be determined by the following tests:

1. With nitrate of silver the formation of a white, curdy precipitate, which does not blacken by exposure to light; it is nearly insoluble in cold nitric acid; when heated to redness it gives off the inflammable vapour of cyanogen.

2. If to the liquid a slight excess of potash be added, then a

mixture of protosulphate and persulphate of iron, a precipitate is occasioned which when treated with excess of hydrochloric acid leaves Prussian blue.

3. Acidulate the liquid with a few drops of hydrochloric acid, place it in a watch glass, and invert over it a second watch glass moistened with a drop of solution of hydrosulphate of ammonia; after a few minutes the upper watch glass is removed, the liquid evaporated to dryness by steam heat, and the dry residue is treated with a drop of solution of sesquichloride of iron; a red sulphocyanide of iron is thus formed; a quantity of hydrocyanic acid not exceeding  $\frac{30}{100}$  of a grain may thus be detected (Dr. A. Taylor).

The cyanides of iron, of cobalt, of chromium, of platinum, and of some other metals, form compounds with the cyanides of the alkalis and of the earths, of a peculiar character, in which the presence of the iron, or of the cobalt, &c., cannot be detected by the usual tests for these metals. Some of these compounds are of considerable importance, and will be noticed at a future point.

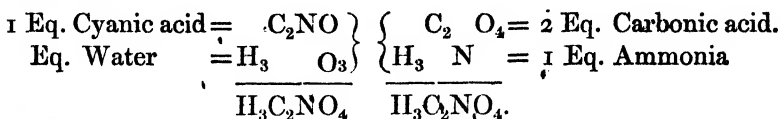
(411) CYANIC ACID, (HO, CyO); *Equivalent*, 9+34. — If cyanogen gas be passed into an alkaline solution, a change ensues something analogous to that which occurs when chlorine is similarly treated, cyanide and cyanate of the base are produced; but the cyanic acid contains only 1 equivalent of oxygen united with 1 of cyanogen;  $2 \text{ Cy} + 2 \text{ KO} = \text{KCyan} + \text{KO, CyO}$ .

Cyanate of potash, however, is better, prepared in a state of purity, by fusing the cyanide of potassium in a crucible and adding litharge (oxide of lead) in small quantities till the oxide ceases to be decomposed;  $\text{KCyan} + 2 \text{ PbO} = \text{KO, CyO} + 2 \text{ Pb}$ . The cyanate is easily separated from the reduced lead and the excess of oxide of lead, which, from their superior density, sink through the melted mass to the bottom. Another method of preparing the cyanate of potash consists in heating an intimate mixture of 2 parts of thoroughly dried ferrocyanide of potassium with 1 part of finely powdered anhydrous peroxide of manganese: the mixture is placed upon a sheet-iron plate and heated to dull redness, and the mass is kept constantly stirred. When the combustion has ceased, cyanate of potash may be dissolved out of the residue with hot alcohol, from which it crystallizes as the solution cools.

Cyanate of potash, if kept dry, may be preserved without change; but so unstable is the cyanic acid when uncombined with a base, that on attempting to separate it from the cyanate of potash by the addition of sulphuric or any other acid, traces of it only are



obtained; a brisk effervescence ensues, each equivalent of the cyanic acid assimilates the elements of water, and is almost entirely resolved into 1 equivalent of ammonia, which remains in combination with the acid employed in decomposing the cyanate, and 2 equivalents of carbonic acid, which escape with effervescence:



Cyanic acid may be otherwise procured: viz., by distilling *cyanuric acid* ( $2\text{HO}, \text{C}_6\text{N}_3\text{HO}_4$ ), which is a crystallizable acid substance, containing exactly the same elements as 3 equivalents of hydrated cyanic acid. When this compound is sealed up in a bent glass tube, one limb of which is kept cool whilst heat is applied to the cyanuric acid in the other limb, a limpid, colourless liquid distils over and is condensed. The cyanuric acid is thus wholly converted into pure hydrated cyanic acid.

Cyanic acid has an extremely pungent odour, and is very volatile; it acts as a powerful caustic if incautiously dropped upon the skin. It is, however, impossible to preserve this compound, as in the course of a few hours it spontaneously changes into a white enamel-like mass, which is permanent in the air, insoluble in water, and destitute of acid properties. To this body the name of *cyamelid* has been given. It has the same composition by weight as the hydrated cyanuric and cyanic acids.

Solutions of the soluble cyanates give white precipitates with solutions of the salts of lead, of silver, or of ~~sub~~oxide of mercury; they yield no precipitate with solution of corrosive sublimate, or with the solutions of salts of iron or of tin.

(412) FULMINIC ACID, not isolable: formula of its salts, ( $2 \text{MO}, \text{N}_2\text{C}_4\text{O}_2$ ).—Besides the remarkable oxides of cyanogen already mentioned, there is another acid which yields on analysis the same percentage of its components as cyanic and cyanuric acids, and cyamelid, though it possesses properties totally different from any of them. Its compounds explode with fearful violence. By dissolving 1 grain of silver in 20 of nitric acid diluted with about 50 grains of alcohol, crystals which contain the new compound are formed, which, when dry, detonate with the slightest friction: they consist of  $2 \text{AgO}, \text{N}_2\text{C}_4\text{O}_2$ . The reaction by which this salt is produced is complicated; the nitrogen however is derived from the nitric acid, and the carbon from the alcohol.

Fulminate of silver may also be formed by transmitting nitrous acid through a saturated solution of nitrate of silver in alcohol; the elements of alcohol and nitrous acid react upon each other, and in the presence of oxide of silver form the fulminate;  $2 \text{NO}_3 + \text{C}_4\text{H}_5\text{O}, \text{HO}=\text{N}_2\text{C}_4\text{O}_2 + 6 \text{HO}$ . The corresponding salt of mercury, when mixed with six times its weight of nitre and made into a paste with water, is used for priming percussion caps; it is somewhat less dangerous than the silver compound, but requires great care in handling. In order to prepare it, one part of mercury is dissolved in 12 of nitric acid, of specific gravity 1.36, and 11 parts of alcohol, of specific gravity 0.850, is added. On applying a gentle heat by means of a water bath a violent reaction commences, nitrous ether is liberated, metallic mercury is deposited, and in a short time opaque minute grains of fulminate of mercury separate, and when cold must be washed with cold water. Boiling water dissolves the salt, and deposits it in fine silky needles, which detonate violently on percussion or on friction between two hard bodies.

Fulminic acid has not been obtained in an isolated form; on attempting to separate it from its salts by a more powerful acid it is resolved into hydrocyanic acid and other bodies.

(413) *Isomerism*.—The properties of these oxides of cyanogen serve clearly to show that mere identity in ultimate composition is not sufficient to produce identity of chemical character or properties; they place the doctrine of *isomerism* (or the existence of compounds identical in ultimate composition, but different in chemical properties) in a striking point of view. Numerous other instances will occur as we pursue further the study of the different compounds, not only of cyanogen, but of other bodies, and particularly of those which form the subject of organic chemistry.

There are various forms of isomerism; in some cases we have no clue to the probable differences of molecular arrangement; in others there is every reason to suppose that the arrangement of the elementary molecules is on a totally different plan in the two bodies which are compared. Hydrated cyanic acid, for instance, may be represented as hydrated oxide of cyanogen; whilst it is certain that in cyamelid, which is insoluble, and presents nothing of the acid character, the arrangement of its constituents is quite different. Isomeric compounds, the equivalent numbers of which are identical, are said to be *metameric*. In other cases, the differences in properties of bodies which contain equal amounts of their constituents in 100 parts, may be simply explained upon the supposition that in the different compounds the state of condensation of these

elements is different; bodies supposed to be thus constituted have been termed *polymeric*.

The following table contains a list of several different polymeric compounds of carbon and hydrogen which contain these two elements in the proportion of single equivalents of each. Each of these bodies, however, possesses properties peculiar to itself; and if equal volumes of the vapour of each be compared, it will be found that the elements have undergone different degrees of condensation in the different compounds. As the density of the vapour increases it has been observed that the boiling point of such as are liquid rises proportionately. Supposing that an equivalent of each compound gives off 4 volumes of vapour, the formulæ will be such as are contained in the subjoined table:—

Substances.	Formula.	Density of vapour.		Boiling point ° F.
		Observed.	Calculated.	
Methylene . . . . .	$C_2H_2$	0.490	0.483	
Olefiant gas . . . . .	$C_4H_4$	0.978	0.967	
Propylene . . . . .	$C_6H_6$		1.451	
Oil gas . . . . .	$C_8H_8$	1.852	1.934	0
Amylene . . . . .	$C_{10}H_{10}$	2.68	2.418	102
Caproylene . . . . .	$C_{12}H_{12}$	2.875	2.902	
Naphthene . . . . .	$C_{16}H_{16}$	3.812	3.868	
Eleene . . . . .	$C_{18}H_{18}$	4.071	4.351	
Paramylene . . . . .	$C_{20}H_{20}$	5.061	4.836	320
Cetylene . . . . .	$C_{32}H_{32}$	8.007	7.736	527
Cerotylene . . . . .	$C_{54}H_{54}$		12.159	
Melissine . . . . .	$C_{60}H_{60}$		14.508	

In this series, olefiant gas has double the density of methylene, and hence it must contain in the same volume of vapour twice as many elementary molecules. In like manner oil gas must contain twice as many molecules as olefiant gas, and four times as many as methylene; naphthene will contain twice as many as oil gas, and cetylene again will contain double the number of particles in the same volume of vapour as naphthene.

(414) PARACYANOGEN, ( $N_2C_6$ ?).—The ordinary operation of preparing cyanogen gas from cyanide of mercury affords a good illustration of this form of isomerism. After the mercury and the cyanogen have been expelled from the glass retort, there always remains a certain quantity of a brown matter, composed of nitro-  
gen and carbon, combined in the same proportions as in cyanogen. Paracyanogen, as this brown body is called, is insoluble in water; it is neither volatile nor fusible, but like cyanogen it enters into combination with other elementary bodies, though the com-

position of these compounds has been as yet but imperfectly studied.

In paracyanogen the carbon and nitrogen are more condensed than in cyanogen; so that if we regard cyanogen as composed of  $\text{NC}_2$ , paracyanogen, according to the experiments of Professor Johnston, would consist of  $\text{N}_3\text{C}_6$ , its equivalent number being three times that of cyanogen, and the elements which compose it being more compactly united.

(4.5) CHLORIDES OF CYANOGEN.—Chlorine forms with cyanogen three isomeric compounds: one is gaseous at the ordinary temperature of the air; the second is liquid, and the third is solid.

The *Gaseous Chloride of Cyanogen*, ( $\text{CyCl}$ ), (*Equivalent*, 61.5, *Specific Gravity*, 2.124,) is colourless: it has an intolerably pungent odour, and irritates the eyes powerfully; at  $0^\circ \text{F}$ . it condenses in long prismatic needles, which fuse at  $5^\circ$ . Four volumes of the gas contain 2 volumes of chlorine and 2 of cyanogen, united without condensation. It dissolves freely in water, ether, and alcohol; the solution has no acid reaction, and does not precipitate nitrate of silver. Gaseous chloride of cyanogen is obtained readily by transmitting a current of chlorine through a retort containing a mixture of powdered cyanide of mercury and water cooled to  $32^\circ$  by immersion in melting ice. Chloride of cyanogen dissolves in the water, and may be expelled by the application of a gentle heat; it may be collected over mercury. According to M. Persoz the gaseous chloride of cyanogen, if liquefied under the pressure of its own vapour, and preserved in tubes hermetically sealed, gradually becomes converted into a crystallized mass of the solid chloride.

*Liquid Chloride of Cyanogen*, ( $\text{Cy}_2\text{Cl}_2$ ), (*Equivalent* 123,) is obtained by exposing cyanide of mercury to the action of chlorine gas in direct sunlight. A yellowish oily liquid is thus obtained which boils at  $61^\circ \text{F}$ ., and is converted into a crystalline mass at  $19^\circ$ . It has an odour resembling that of the gaseous chloride. Liquid chloride of cyanogen does not mix with water, but dissolves freely in alcohol.

*Solid Chloride of Cyanogen*, ( $\text{Cy}_3\text{Cl}_3$ ); *Equivalent*, 184.5.—This substance crystallizes in white needles. It has a disagreeable odour, like that of mice. Chloride of cyanogen melts at  $284^\circ$ , and boils at  $374^\circ$ . The specific gravity of its vapour, according to Bineau, is 6.39; in this compound, therefore, 6 volumes of chlorine and 6 volumes of cyanogen are condensed into 4 volumes. This chloride is but sparingly soluble in water, though it is freely taken up by alcohol and ether. It is very poisonous. The solid chloride

of cyanogen may be prepared by decomposing concentrated hydrocyanic acid by exposing it in a glass vessel with an excess of dry chlorine to the direct rays of the sun.

Bromine and iodine form solid crystalline compounds with cyanogen, corresponding in composition with the gaseous chloride; they may be obtained by distilling cyanide of mercury with bromine or with iodine.

(416) There are other important compounds of cyanogen, the consideration of which will be more advantageously pursued hereafter; it will be sufficient at this point to indicate some of their leading chemical peculiarities.

Cyanogen, as we have seen, enters into combination with the non-metallic elements as though it were itself an elementary body. In this manner bodies such as the chlorides, the bromides, and the iodides of cyanogen may be obtained; they form well-defined compounds, which do not exhibit any special tendency to unite with other elements. In other cases, however, it is important to observe that many of the compounds to which cyanogen gives rise are themselves endowed with the property, of uniting again, as though they were simple bodies, with other elements. With sulphur, for example, cyanogen forms a bisulphide ( $\text{NC}_2\text{S}_2$ ), which, in combination with the metals, performs the part of a compound radicle, usually termed sulphocyanogen ( $\text{Scy}$ ), and which produces a series of salts, termed sulphocyanides, many of which may be crystallized; of this the sulphocyanide of potassium,  $\text{K, NC}_2\text{S}_2$  or  $\text{K Scy}$ , furnishes an instance. Similar compound radicles are furnished also by the union of cyanogen with many of the metals themselves; in this way iron in the ferrocyanides, and cobalt and chrome in the cobaltcyanides and chromocyanides, form each a compound group, or salt radicle, which, when it unites in its turn with other metals, performs the functions of a simple body, such as chlorine or iodine; an example of this is seen in the well known prussiate of potash, or as it is usually termed, ferrocyanide of potassium, ( $\text{K}_2, \text{Fe Cy}_3$ ), in which the compound of iron and cyanogen,  $\text{FeCy}_3$ , is considered as a compound radicle ( $\text{Fcy}$ ).

#### § V. GENERAL REMARKS ON THE DISCRIMINATION OF THE GASES FROM EACH OTHER.

(417) Having now described all the gaseous compounds which are of any considerable importance, with the exception of two—viz., arseniuretted hydrogen and telluretted hydrogen, it will be advan-

tageous to take a brief review of their general characters before passing to the consideration of the metals and their compounds.

There are about thirty bodies which are permanently gaseous at the mean temperature of the atmosphere. Several of these compounds are met with in the uncombined form in the atmosphere, either uniformly, or under particular circumstances not of unfrequent occurrence: these gases are oxygen, nitrogen, carbonic acid, sulphurous acid, hydrosulphuric acid, ammonia, and occasionally carbonic oxide and light carburetted hydrogen. Generally speaking, the different gases, when pure, are readily distinguished from each other by some well marked physical or chemical property. The few gases which are coloured are at once indicated by the peculiarity of their tint, conjoined with their characteristic odour; in this manner peroxide of nitrogen, chlorine, hypochlorous acid, chlorous acid, peroxide of chlorine, and bromine vapour are at once recognised.

Many gases have a peculiar and characteristic odour. Some of the most important, however, including oxygen, nitrogen, hydrogen, carbonic acid, carbonic oxide, light carburetted hydrogen, olefiant gas, and protoxide of nitrogen, are destitute of odour, and require other means for discriminating them from each other.

(418) In order to aid the operator in distinguishing the different gases from each other, Thénard divided them into four groups, the arrangement being dependent upon the action of a solution of potash upon them, conjoined with the occurrence or the absence of combustion on the application of a lighted match to the gas. The action of potash is ascertained by admitting a few drops of a solution of potash into a test tube filled with the gas, and standing over mercury; on agitating the contents of the tube, it is immediately obvious whether any absorption occurs. The application of a lighted match to another small tube filled with the gas shows whether it be inflammable, or whether it extinguishes or supports combustion.

The four groups of gases which are formed by the application of these tests are the following:—

1. Gases which are absorbable by potash, but which are not inflammable.
2. Gases absorbable by potash, but which are inflammable.
3. Gases insoluble in potash, not inflammable.
4. Gases insoluble in potash, which are inflammable.

We proceed to point out briefly the characters of the components of each group.

(419) 1. *Gases which are absorbable by potash, but are not inflammable*; these are 15 in number:—viz.,

- |                        |                           |
|------------------------|---------------------------|
| 1. Hydrochloric acid   | 9. Nitrous acid           |
| 2. Hydrobromic acid    | 10. Peroxide of chlorine  |
| 3. Hydriodic acid      | 11. Chlorous acid         |
| 4. Fluoride of silicon | 12. Hypochlorous acid     |
| 5. Fluoride of boron   | 13. Chlorine              |
| 6. Chloride of boron   | 14. Carbonic acid         |
| 7. Chlorocarbonic acid | 15. Chloride of cyanogen. |
| 8. Sulphurous acid     |                           |

Of these gases each of the first eleven reddens litmus paper, when moistened and plunged into it. Hypochlorous acid and chlorine destroy its colour, and bleach it entirely. Carbonic acid is nearly without action, and chloride of cyanogen produces no effect upon its colour. The first six gases fume strongly when mixed with the air, owing to their action on the moisture which it contains: the solutions in water of hydrochloric, hydrobromic, and hydriodic acids are immediately distinguished by the usual tests. Each gas also presents certain peculiarities, viz.—1. A small quantity of chlorine produces no change in the hydrochloric gas; 2. In hydrobromic gas it occasions the separation of red fumes of bromine; and 3. In the hydriodic gas violet fumes of iodine appear. 4. Fluoride of silicon is recognised by the gelatinous deposit of silica which water produces when the gas dissolves in this liquid. 5. The fluoride of boron produces a gelatinous precipitate in the solution of potash, but not in pure water. 6. Chloride of boron is decomposed by water into hydrochloric and boracic acids, which may be recognised in the solution by the appropriate tests. 7. Chlorocarbonic acid has a peculiar, pungent odour, and is decomposed by water into hydrochloric and carbonic acids. 8. Sulphurous acid is immediately recognised by the suffocating odour of a sulphur match: it is absorbed by the peroxide of lead, and a white sulphate of lead is formed. 9. Nitrous acid is sufficiently characterized by its colour and peculiar odour; and, 10. the same may be remarked of peroxide of chlorine. 11. Chlorous acid has a greener tinge than the peroxide of chlorine, and it yields a bright yellow solution when dissolved in water. 12. Hypochlorous acid has the odour of the bleaching compounds of chlorine with the alkalis and earths, and it rapidly destroys vegetable colours: these three oxides of chlorine detonate by the application of a temperature below that of boiling water. 13. Chlorine is distinguished by its green colour,

remarkable odour, by its bleaching action on vegetable colours, and by its sparing solubility in water, which takes up about twice its bulk. 14. Carbonic acid extinguishes flame, renders lime-water turbid, and dissolves in about its own bulk of water. 15. Chloride of cyanogen is recognised by its pungent odour, and its peculiar irritating effect on the eyes.

(420) 2. *Gases absorbable by Potash, and inflammable*; these are only 4 in number:—viz.,

- |                           |                         |
|---------------------------|-------------------------|
| 1. Sulphuretted hydrogen. | 3. Telluretted hydrogen |
| 2. Seleniuretted hydrogen | 4. Cyanogen.            |

These gases are recognised with great facility. 1. Sulphuretted hydrogen has a peculiar odour of putrid eggs; it burns with a blue flame, often attended with a deposit of sulphur: it blackens paper soaked in a solution of acetate of lead, and is decomposed by moist chlorine, with separation of sulphur; water dissolves about twice its bulk of the gas. 2. Seleniuretted hydrogen has an odour analogous to that of the preceding gas; its aqueous solution gradually deposits selenium in the form of a red amorphous precipitate: it precipitates salts of zinc of a flesh red colour. 3. Telluretted hydrogen is also decomposed by chlorine, metallic tellurium subsiding as a brown powder. 4. Cyanogen burns with a rose-edged purple flame; it has a penetrating characteristic odour. If mixed with an equal volume of oxygen, and a red hot platinum wire be suspended in the mixture, red nitrous fumes are produced by the oxidation of the nitrogen contained in the gas.

(421) 3. *Gases not absorbable by Potash, and not inflammable*; of these also there are four—viz.,

- |                          |                           |
|--------------------------|---------------------------|
| 1. Oxygen                | 3. Nitrogen               |
| 2. Protoxide of nitrogen | 4. Deutoxide of nitrogen. |

1. Oxygen is at once distinguished from all other gases by its property of kindling a glowing match, by its power of producing red fumes when mixed with deutoxide of nitrogen, and by its insolubility in water when agitated with it. 2. Protoxide of nitrogen, though it rekindles a glowing match, dissolves when agitated with water. 3. Nitrogen extinguishes the flame of burning bodies; it is insoluble in water, and does not render lime-water turbid. 4. Deutoxide of nitrogen is instantly recognised by the red fumes which it occasions when mixed with air or free oxygen; it is immediately absorbed by a solution of protosulphate of iron, giving the liquid a deep brown colour.



(422) 4. *Gases not absorbable by Potash, which are inflammable*; these gases are seven in number:—viz.,

- |                               |                           |
|-------------------------------|---------------------------|
| 1. Hydrogen                   | 5. Phosphuretted hydrogen |
| 2. Light carburetted hydrogen | 6. Arseniuretted hydrogen |
| 3. Olefiant gas               | 7. Carbonic oxide.        |
| 4. Oil gas                    |                           |

1. Hydrogen is inodorous, if pure; it burns with a feebly luminous flame, and if mixed with half its volume of oxygen produces water, either by the transmission of an electric spark, or by the action of a ball of spongy platinum. 2. Light carburetted hydrogen burns with a luminous flame; it is not acted upon if mixed with chlorine over water, and is not dissolved by fuming sulphuric acid. 3. Olefiant gas, when mixed with an equal volume of chlorine, even in the dark condenses to an oily liquid which is insoluble in water; it is also absorbed by perchloride of antimony, and by the Nordhausen sulphuric acid. It burns with a brilliant smoky flame. 4. Oil gas is soluble in oil of vitriol, and in alcohol; it burns with a brilliant smoky flame. When the last two gases are mixed together, there is considerable difficulty in identifying the existence of each in such a mixture. 5. Phosphuretted hydrogen is distinguished by its peculiar alliaceous odour. It burns with a luminous flame, producing white fumes of phosphoric acid; solutions of the salts of copper, silver, and mercury dissolve it, and form brown precipitates. 6. Arseniuretted hydrogen is decomposed if passed through glass tubes heated nearly to redness, a ring of metallic arsenic being deposited. It burns with a peculiar whitish flame, and deposits a brown stain of metallic arsenic on cold bodies introduced into the burning jet. It is extremely poisonous, and has a peculiar odour of garlic. 7. Carbonic oxide burns with a pale blue flame, producing carbonic acid. It is insoluble in water, and dissolves in a solution of dichloride of copper in hydrochloric acid.

In a mixture of gases a qualitative examination must be made as a preliminary step in order to ascertain what gases are present. It is of course needless to search for those which mutually condense or decompose each other. Thus ammonia would not be found in a mixture which contained hydrochloric, hydriodic, hydrobromic, sulphurous, or nitrous acid gases. Oxygen would not occur in a mixture in which binoxide of nitrogen was present. Neither could free chlorine or its oxides co-exist with hydriodic or hydrobromic acid, or with olefiant gas, or with the compounds of hydrogen with sulphur, selenium, tellurium,

phosphorus, or arsenic: chlorine and its oxides are equally incompatible with ammonia.

(423) *General Principles of the Analysis of a Mixture of Gases.* The complete analysis of a mixture of different gases is one of the most delicate and difficult branches of chemical analysis, and it is not intended on the present occasion to attempt to give more than an idea of the principles on which such an operation is conducted, and of the apparatus by which it is effected.

As an illustration of the method of proceeding we may take a case of frequent occurrence: viz., the determination of the composition of a sample of coal gas. In this gas, the ingredients which may be present are numerous. These are—1, hydrogen; 2, olefiant gas and other hydrocarbons; 3, light carburetted hydrogen; 4, carbonic oxide; 5, carbonic acid; 6, sulphuretted hydrogen; 7, ammonia; 8, oxygen, and 9, nitrogen derived from the atmosphere.

A qualitative examination is made thus;—the proportion of ammonia and of sulphuretted hydrogen is usually very minute, and in most cases these gases must be sought for by placing the tests for their presence for some time in a current of the coal gas. In searching for ammonia, a piece of moistened litmus paper, feebly reddened, is placed for a minute in a jet of the issuing gas. If the blue colour be restored, ammonia is present. Paper soaked in a solution of acetate of lead may be subjected to a similar trial. If it turn brown, sulphuretted hydrogen is present. The presence of oxygen is detected by admitting a bubble of the deutoxide of nitrogen into a tube filled with the gas under trial, and looking through the tube obliquely upon a sheet of white paper; very small traces of oxygen may thus be detected by the red tinge produced, owing to the formation of peroxide of nitrogen. Carbonic acid may be detected by the turbidity which it produces in lime-water or in a solution of sub-acetate of lead, if thrown up into the gas, whilst standing in a tube over mercury. The existence of the other gases may be assumed, as they are certain to be present in greater or less quantity. The sulphuretted hydrogen and ammonia being too small in amount to be quantitatively determined, and supposing that oxygen and carbonic acid are found to be present, the proportion of seven different gases will remain to be ascertained. The following method may be adopted for their quantitative determination:

1. *Carbonic Acid.*—A volume of the gas is confined over mercury, and its bulk is measured, with due attention to temperature and pressure. A piece of caustic potash which has been melted

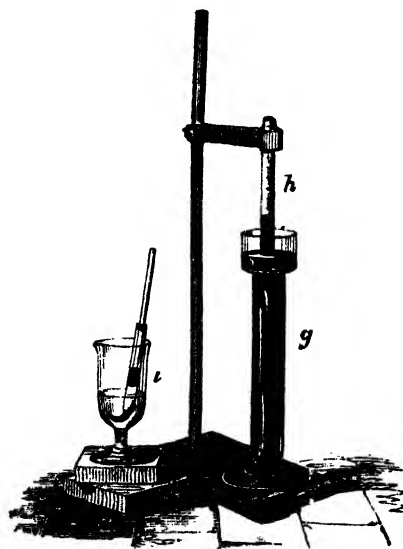
upon the end of a long platinum wire, to serve as a handle, is introduced from below, through the mercury into the tube. After two or three hours the potash is withdrawn, the amount of the absorption indicates the proportion of carbonic acid which was present.

2. *Olefiant Gas and Heavy Hydrocarbons.*—These gases are absorbed by introducing another ball, consisting of porous coke moistened with fuming sulphuric acid. It is necessary, however, before reading off the volume of the gas, to introduce a ball of potash a second time, to withdraw the vapour of anhydrous sulphuric acid, which possesses sufficient volatility to introduce a serious error by dilating the bulk of the gas, unless it be completely removed. The total amount of absorption will indicate the proportion of olefiant gas, together with the vapours of condensable hydrocarbons.

3. *Oxygen.*—This gas is determined in a similar manner, by employing a ball of phosphorus, which must be left in the gas for twenty-four hours; the fresh diminution in bulk, shows the proportion of oxygen.

4. *Carbonic Oxide.*—The accurate separation of carbonic oxide from the other gases is not easily effected. The gas may be divided

FIG. 282.



into two portions, one of which is to be carefully measured as it stands over mercury, in the jar, *h*, fig. 282; a small quantity of a solution of subchloride of copper in hydrochloric acid is next added by means of the syringe, *i*, and the mixture is briskly agitated; the gas is then withdrawn by means of the gas pipette shown in fig. 243, p. 478, and transferred by its means to a second graduated tube, also standing over mercury; into this tube a ball of potash on the end of a platinum wire is introduced, for the purpose of absorbing the vapours of hydrochloric acid with which the gas is saturated; its

bulk may then be read off, and the volume of carbonic oxide may be known by the loss in bulk which it has experienced.

5, 6, 7. *Nitrogen, Carburetted Hydrogen, and Hydrogen.*—The determination of the carbonic oxide, however, may be effected without having recourse to absorption; along with the carburetted hydrogen and hydrogen. Let a portion of the gas in which the carbonic oxide is still present be now transferred to a syphon eudiometer (fig. 239), and let its bulk,  $V$ , be accurately measured: then add about twice its volume of oxygen, and measure the gas a second time: let this bulk be  $V_1$ ;  $V_1 - V$  will give the volume of oxygen which has been added. Let  $V_2$  be the bulk of the gas after the mixture has been exploded by the transmission of the electric spark:  $V_1 - V_2$  indicates the diminution in bulk which it has experienced: call this  $a$ . Then inject a small quantity of a strong solution of potash, and again note the volume,  $V_3$ . The absorption,  $V_2 - V_3$ , will be due to the quantity of carbonic acid which has been formed: call this  $b$ . The remaining gas,  $V_3$ , consists of oxygen in excess, and nitrogen. The quantity of oxygen in excess is ascertained by mixing the residual gas with about twice its bulk of hydrogen, and causing the electric spark to pass a second time. Let the volume of the mixture before firing be  $V_4$ , and let  $V_5$  be the bulk after firing:  $V_4 - V_5$  will represent the amount of condensation; and one-third of this, or  $\frac{V_4 - V_5}{3}$  will be due to the excess of oxygen. On deducting this from the residue,  $V_3$ , the difference gives the volume of nitrogen,  $n$ ;  $V_3 - \frac{V_4 - V_5}{3} = n$ . The difference between the amount of the oxygen thus found to be in excess, and that originally introduced, will of course represent the quantity of oxygen consumed: call this  $c$ : thus  $V_1 - V - \frac{V_4 - V_5}{3} = c$ .

We have now all the data for calculating the proportion of carburetted hydrogen, of hydrogen, and of carbonic oxide, which are present in the mixture.

Let  $x$  represent the quantity of light carburetted hydrogen; this gas requires twice its own volume of oxygen for complete combustion, and furnishes its own volume of carbonic acid, which requires for its formation an equal volume of oxygen, or half the amount consumed; the other half of the oxygen being required by the hydrogen which condenses in the form of water;  $2x$  will be the diminution in bulk of oxygen which occurs on detonation (401).

Again, when hydrogen is converted into water, it requires half its bulk of oxygen, and both are condensed entirely. If  $y$  represent the bulk of the hydrogen,  $\frac{3y}{2}$  will be the diminution in bulk of the mixed gases on detonation, which is occasioned by the hydrogen in the mixture.

Let  $z$  represent the volume of carbonic oxide present; carbonic

oxide, for conversion into carbonic acid, requires half its bulk of oxygen, the carbonic acid produced occupying the same bulk as the carbonic oxide.  $\frac{z}{2}$  will therefore indicate the condensation which occurs on firing the mixture.

The total condensation in bulk,  $a$ , which occurs on firing a mixture of light carburetted hydrogen, hydrogen, and carbonic oxide will consequently admit of being thus represented :—

$$(1) \quad a = 2x + \frac{3y}{2} + \frac{z}{2}$$

Further, the quantity of the carbonic acid formed by the detonation,  $b$ , is composed of a volume of carbonic acid equal in bulk to the light carburetted hydrogen, and a volume equal to that of the carbonic oxide, so that the total quantity of carbonic acid may be thus indicated :—

$$(2) \quad b = x + z$$

And lastly, the oxygen consumed,  $c$ , will be composed of the following quantities : by light carburetted hydrogen, twice its bulk,  $2x$ ; by hydrogen, half its bulk,  $\frac{y}{2}$ ; and by carbonic oxide, half its bulk,  $\frac{z}{2}$ ; or the total quantity of oxygen consumed will be the following :—

$$(3) \quad c = 2x + \frac{y}{2} + \frac{z}{2}$$

From these three equations the values of  $x$ ,  $y$ ,  $z$ , are determined :—

$$x = c - \frac{a+b}{3}$$

$$y = a - c$$

$$z = \frac{a+b}{3} - c$$

Minute directions for the analysis of various gaseous mixtures are given by Regnault, in the fourth volume of his *Cours Élémentaire de Chimie*, which contains a description of a form of eudiometer well adapted for accurate experiments. Bunsen has also introduced very important improvements in the manipulation and apparatus required for the analysis of gases. (See an article on Eudiometry, by Kolbe, in Liebig and Poggendorff's *Handwörterbuch der Chemie*, vol. ii.)

## CHAPTER X.

## THE METALS.

## § I. GENERAL PROPERTIES OF THE METALS.

(424) THE metals, as a class, are characterized by a peculiar lustre, termed the metallic lustre. They are possessed of a high degree of opacity, and are good conductors both of heat and electricity. Some of them are also endowed with the properties of ductility, or fitness for drawing into wire, and of malleability, or extensibility under the hammer. Most of them have a high specific gravity. When separated from their compounds by electrolytic action, they appear at the platinode, or negative wire of the voltaic battery.

These properties are not developed equally in all the metals; in some metals one or more of them may be wanting altogether: and there are other substances, not metallic in their nature, in which some of these characters are strongly displayed.

(425) *Lustre, Opacity, and Colour.*—Although, when polished, all metals present the lustre termed metallic, yet most of them may be obtained by minute subdivision in a form devoid of lustre. Iron, copper, platinum, gold, silver, and even mercury may be thus readily procured by processes to be mentioned hereafter.

If, however, these metallic powders be subjected to pressure under the burnisher, a sufficient approximation of their particles is produced to render them capable of reflecting light, and the metallic lustre re-appears. This property admits of being applied in the fine arts: for instance, it is possible to make copies of medals or ancient coins, by employing finely divided copper, which is introduced with the medal into a mould: by submitting it to pressure an exact copy of the medal, with a beautifully polished surface, is obtained: the copy is then strongly heated, care being taken to exclude atmospheric air: during the ignition the copy shrinks a little in all directions, but a fac-simile is formed, which is extremely distinct, though reversed, and a little smaller than the original.

Bodies which are not metallic occasionally assume a brilliant surface like the metals. Iodine, which in all its chemical relations is directly opposed to the metals, yet possesses a strong lustre; the

same thing is observable in a form of charcoal, termed by the workmen *kish*, which escapes from the vent-holes of the moulds during the process of casting iron. A native form of carbon,—graphite or plumbago, has received its popular name of *black-lead* from its metallic appearance.

Metals are among the most opaque bodies with which we are acquainted; but their opacity is not perfect. When reduced to exceedingly fine leaves, a portion of light is transmitted; thus pure gold, of not more than  $\frac{1}{100000}$  inch thick, allows a purple light to pass.

The colour of the reflected light varies with the nature of the metal. In most cases it is nearly white, with a shade peculiar to each metal: the tints of silver, platinum, tin, cadmium and palladium, are nearly alike; other metals, as lead and zinc, have a bluish colour; others, like iron and arsenic, have a greyish hue; calcium and barium are pale yellow; gold is a full yellow; and copper is of a red colour. By repeated reflections from the same metal a distinct colour is rendered obvious, which was not seen upon looking at the polished surface. A red tint may thus be made evident in silver, and a violet tinge in steel.

Some of the metals possess a characteristic odour: iron and copper emit, on friction, a smell peculiar to themselves, and arsenic, when volatilized, evolves a powerful odour of garlic. The taste of most of the soluble compounds of the metals is astringent or acid, and of the peculiar kind termed metallic.

(426) *Hardness, Brittleness, and Tenacity*.—Great differences are observable between the hardness of the different metals; steel may be rendered hard enough to scratch glass, while lead will take impressions from the finger-nail, and potassium may be spread like butter.

Many of the harder metals are very elastic and sonorous when struck; but these properties are more strikingly displayed in some of the alloys, or compounds of the metals with each other, as in the alloy of tin and copper used for bells, and in the combination of carbon with iron, well known as steel, which, by its high elasticity, is pre-eminently qualified for the construction of the springs used in machinery.

Closely connected with the hardness are the *brittleness* and the *tenacity* of metals, which are very variable. Some, like antimony, arsenic, and bismuth, may be pulverized without difficulty in a mortar, while others, as iron, gold, silver, and copper, require great force to effect their disintegration. The brittleness of some of the metals

is materially affected by temperature. Zinc, within the ordinary atmospheric range, is so brittle that it cannot be bent at a sharp angle without danger of destroying its cohesion, while if heated to between  $200^{\circ}$  and  $300^{\circ}$  F., it may be wrought with facility. Brass, an alloy of copper and zinc, on the contrary, becomes brittle at temperatures approaching to redness, but while cold it possesses considerable malleability.

Taking the tenacity of lead = 1, the tenacity of the different metals, after annealing, will be represented according to Wertheim's experiments as follows:—

Lead . . . . .	1	Silver . . . . .	8.9
Cadmium . . . . .	1.2	Platinum . . . . .	13
Tin . . . . .	1.3	Palladium . . . . .	15
Gold . . . . .	5.6	Copper . . . . .	17
Zinc . . . . .	8	Iron . . . . .	26

The tenacity of the metals has been measured by fixing firmly in a vice one end of a bar or wire of the metal, the strength of which is to be ascertained, and attaching to the other a convenient support for weights which are cautiously increased until the wire breaks. By comparing together the weights required to determine the rupture of the different metals for bars of equal section, a comparative table of tenacity may be formed. Various circumstances materially influence the strength of the same metal; such as its purity, the mode in which the bar has been prepared (whether by casting, by forging, or by wire-drawing), the temperature at which the comparisons are made, the application or omission of the process of annealing, and the manner in which the tension has been exerted, whether gradually or suddenly. Different observers, in consequence of operating differently in some one or other of these respects, have obtained results which vary from each other considerably. The necessity of attention to these points will be evident on examining the results obtained by M. Wertheim (*Ann. de Chimie*, III. xii. p. 440), who has given an elaborate series of experiments upon the tenacity of different metals, the most important of which are embodied in the following table. The numbers represent the weight in kilogrammes which a bar of each metal of 1 millimetre square would support without breaking, both when the strain is gradually increased and when suddenly applied:—



	60° F.		212° F.	392° F.
	Gradual.	Sudden.		
Cast steel, drawn . . . . .		83·8		
Do. do., annealed . . . . .	65·7			
Piano wire, (steel) . . . . .	70·0	99·1		
Do., annealed . . . . .	40·0	53·9	59·10	50·90
Iron wire . . . . .	61·10	65·1		
Do., annealed . . . . .	46·88	50·25	51·10	46·9
Copper wire . . . . .	40·30	41·0		
Do., annealed . . . . .	30·54	31·63	22·10	
Platinum wire . . . . .	34·10	35·0		
Do., annealed . . . . .	23·50	27·70	22·60	19·70
Palladium wire . . . . .		27·2		
Do., annealed . . . . .	27·4			
Silver wire . . . . .	29·0	29·6		
Do., annealed . . . . .	16·02	16·5	14·00	14·00
Zinc, commercial, drawn . . . . .	12·80	15·77		
Do. do., annealed . . . . .		14·40	12·20	7·27
Pure zinc, cast . . . . .	4·5			
Gold, drawn . . . . .	27·0	28·4		
Do., annealed . . . . .	10·08	11·1	12·60	12·00
Cadmium, drawn . . . . .	2·24			
Do., annealed . . . . .		4·81	2·60	
Lead, cast . . . . .	1·25	2·21		
Do., drawn . . . . .	0·7	2·36		
Do., annealed . . . . .	1·80	2·04	0·54	
Tin, drawn . . . . .	2·45	3·0		
Do. do., annealed . . . . .	1·70	3·62	0·85	

It will be seen from an inspection of this table, that the general effect of heat is to diminish the tenacity of the metals, except in the case of iron, steel, and gold, the tenacity of which seems to be somewhat increased by a heat of 212°; this is particularly so with iron; by a further elevation of temperature the tenacity again diminishes. The influence of annealing, or heating the bar to dull redness and allowing it slowly to cool, is still more remarkable, for by this means the tenacity of gold is reduced more than half, that of silver nearly as much, that of platinum about one-third, and that of iron and copper about a fourth.

(427) *Malleability and Ductility*.—The following metals are termed malleable metals, *i e.*, metals which may be reduced to thin leaves either by lamination between rollers, or by hammering:—

Gold	Iron
Silver	Tin
Copper	Lead
Platinum	Cadmium
Palladium	Nickel
Aluminum	Cobalt.
Zinc	

Frozen mercury, as well as lithium, potassium, and sodium, likewise admits of extension under the hammer. Gold far surpasses all the other metals in malleability, being capable of reduction into leaves so thin that a square foot weighs less than three grains; and the film does not exceed the 200,000th of an inch in thickness. Silver and copper may also be reduced to leaves of great tenuity. The others may be rolled into foil, but cannot be hammered into leaf. At the Industrial Exhibition of Breslau, 1852, an album of leaf iron was exhibited, the sheets of which did not exceed the 25,000th of an inch in thickness, and a square inch of the leaf weighed only three-fourths of a grain. Nickel and cobalt, however, are far inferior to the other metals in the list. The metals become denser in rolling, and are often rendered so hard that they require to be annealed between every second or third rolling. During the process of hammering or rolling, much heat is extricated.

The metals may be arranged in the following order of ductility, the property being most marked in those which are first mentioned :—

Iron	Calcium
Copper	Nickel
Silver	Zinc
Gold	Tin
Platinum	Lead
Palladium	Lithium.

Ductility is peculiarly displayed by the first seven metals on the list. Dr. Wollaston procured a wire of platinum, the diameter of which did not exceed the 30,000th of an inch, by placing a wire of platinum in the axis of a small cylinder of silver, and reducing the compound wire to the utmost practicable tenuity in the ordinary way, by drawing it through holes made in a hard steel plate, termed a draw-plate; the apertures through which the wire was made to pass diminishing in size by regular gradation. Both metals were thus attenuated, *pari passu*, and the silver was finally dissolved off by nitric acid, which left the platinum unacted upon. Steel wires of extreme fineness have been produced in a similar manner, the silver being, in this case, dissolved by the action of mercury. Zinc, tin, lead, and even lithium, may also be obtained in the form of wire, but with difficulty, on account of their feeble tenacity.

The malleability of a metal is by no means always proportioned to its ductility: iron, though it may be reduced to wires of ex-

treme fineness, is not nearly so malleable as gold, silver, copper, and some other metals which are inferior to it in ductility. A few substances which are not metallic exhibit, when in a state of semifusion, a very perfect ductility. Half-melted glass shows this property in a marked degree; it may be spun into very fine threads, which have even been woven into a species of cloth, designed for ornamental purposes.

It is obvious that the properties of brittleness, tenacity, ductility, and malleability, must be materially dependent upon the texture of the metal. This is strikingly exemplified in the variation in tenacity exhibited by the same metal under different circumstances. Silver, in ordinary cases, is tough, ductile, and malleable; by repeated heatings and coolings, however, its particles arrange themselves in a crystalline manner, and it then becomes very brittle. Copper, when deposited in crystals by slow voltaic action, is very hard and brittle; but when the action is more rapid it is soft and tough, and then exhibits a fibrous character: and it may be stated, as a general principle, that the crystalline metals, such as zinc, antimony, bismuth, and arsenic, are the most brittle; while those which, like iron, have a fibrous structure, are possessed of a high degree of tenacity.

The structure of a metal is easily displayed in many cases by placing it in solvents, the operation of which is very gradual. Some of the metals which fuse readily may be obtained in crystals without difficulty, by allowing a few pounds of the melted metal to cool slowly, and pouring out the interior portions before the whole has had time to solidify; the inner walls of the cavity are then found to be lined with crystals. Bismuth is particularly well adapted to this process. The less fusible metals, such as copper, iron, and silver, may often be crystallized from their solutions by slow voltaic actions. Many of them, as, for example, gold, silver, and copper, occur native in crystals. A large proportion of the metals crystallize in forms belonging to the regular system.

(428) *Specific Gravity*.—Wide differences are observable in the specific gravity of the metals. In the annexed table variations are exhibited between the extremes of iridium and platinum, the heaviest known forms of matter, on the one hand, and lithium on the other, which has little more than half the density of water. The lighter metals are all characterized by their powerful affinity for oxygen; those which are least oxidizable possessing generally the highest specific gravity. In a few instances, the most marked of which is platinum, the density may be somewhat increased by rolling and hammering; but this is not usually the case.

*Specific Gravity of the Metals.*

Metal.	Sp. Gr.	Observer.
Platinum . . . .	21'5	Wollaston.
Gold . . . .	19'34	G. Rose.
Tungsten . . . .	17'6	D'Elhuyart.
Mercury . . . .	13'596	Regnault.
Palladium . . . .	11'8	Wollaston.
Lead . . . .	11'44	Berzelius.
Silver . . . .	10'53	G. Rose.
Bismuth . . . .	9'799	Marchand and Scheerer.
Cobalt . . . .	8'95	Rammelsberg.
Copper . . . .	8'92	Marchand and Schoerer.
Nickel . . . .	8'82	Tupputi.
Molybdenum . . . .	8'62	Bucholz.
Cadmium . . . .	8'604	Stromeyer.
Manganese . . . .	8'013	John.
Iron . . . .	7'844	Broling.
Tin . . . .	7'292	Kupffer.
Zinc . . . .	7'146	Wertheim.
Antimony . . . .	6'71	Marchand and Scheerer.
Tellurium . . . .	6'25	Berzelius.
Arsenic . . . .	5'969-5'7	Guibourt.
Chromium . . . .	5'9	Richter.
Aluminum, rolled . . . .	2'67	Deville.
cast . . . .	2'56	Deville.
Strontium . . . .	2'54	Bunsen.
Glucinum . . . .	2'1	Debray.
Magnesium . . . .	1'743	Bunsen.
Calcium . . . .	1'578	Bunsen.
Sodium . . . .	0'972	Gay Lussac and Thénard.
Potassium . . . .	0'865	Gay Lussac and Thénard.
Lithium . . . .	0'593	Bunsen.

(429) *Fusibility*.—The melting points of the different metals differ not less widely than their densities. Mercury, for instance, remains fluid as low as  $-39^{\circ}$  F., while platinum, iridium, rhodium, and several others, require the intense heat of the voltaic battery, or of the oxyhydrogen blowpipe to effect their fusion :

*Order of Fusibility of the Metals.*

	$^{\circ}$ F.	$^{\circ}$ C.	
Mercury . . . .	-39	-39'4	Hutchins.
Potassium . . . .	136	58	} Gay Lussac and Thénard.
Sodium . . . .	190	88	
Lithium . . . .	356	180	
Tin . . . .	442	228	Crichton.
Bismuth . . . .	507	264	Rudberg.
Lead . . . .	617	325	Rudberg.
Cadmium . . . .	} undetermined.		
Tellurium . . . .			
Arsenic . . . .			
Zinc . . . .	773	412	Daniell.
Antimony . . . .	below redness.		
Calcium . . . .	} above a red heat.		
Aluminum . . . .			

	° F.	° C.	
Silver . . . .	1873 . .	1023 . .	} Daniell.
Copper . . . .	1996 . .	1091 . .	
Gold . . . .	2016 . .	1102 . .	
Cast iron . . . .	2786 . .	1530 . .	
Cobalt . . . .	} highest heat of forge.		
Nickel . . . .			
Wrought iron . . . .			
Manganese . . . .			
Molybdenum . . . .	} agglomerate, but do not fuse in the forge.		
Tungsten . . . .			
Chromium . . . .			
Palladium . . . .			
Platinum . . . .	} require the heat of the oxyhydrogen blowpipe.		
Rhodium . . . .			
Iridium . . . .			
Vanadium . . . .			

Some metals near their melting points, before undergoing complete fusion, pass through a soft, intermediate stage, in which, if two clean surfaces be presented to each other, and strong pressure or hammering be employed, they unite, or weld together, so as to form one continuous mass. Iron, lithium, and potassium afford the most striking instances of this. Palladium is also, in a minor degree, susceptible of it.

(430) *Volatility*.—Many of the metals admit of being volatilized without difficulty. Mercury, when heated under ordinary atmospheric pressure, boils, and is reduced to a perfectly colourless transparent vapour, at about 662° F. It is important to observe that this dry vapour, though metallic, is an insulator of electricity, and will allow the transmission of distinct electric sparks as readily as atmospheric air. The insulating power of mercurial vapour on the one hand, and the small specific gravity of potassium, of sodium, and of lithium on the other, show that there is nothing inconsistent with facts in the supposition that hydrogen itself, although the lightest known form of matter, and though gaseous, and consequently an insulator of electricity, may possibly be a metal; and indeed, in its chemical properties, it approximates very closely to this class of bodies. The seven metals named below are sufficiently volatile to be distilled from the compounds from which they are obtained: those which require the smallest amount of heat stand first:

Mercury  
Arsenic  
Tellurium  
Cadmium

Zinc  
Potassium  
Sodium.

Arsenic is volatilized below redness, and even before it has assumed

the liquid form. Cadmium requires a dull red heat, and zinc a higher temperature. Those metals which are generally considered fixed in the fire are likewise volatilizable to a certain extent. In the process of lead smelting, one-seventh of the lead escapes up the chimney, and would be wasted unless means for collecting it were adopted. Even copper is not absolutely fixed in the fire. My friend, Dr. Percy, some years ago showed me a remarkable illustration of this fact: he has in his possession part of a beam which, for many years, was suspended over a furnace in a copper smelting house in Norway; the whole beam, of which this is a fragment, contains minute beads of metallic copper studded through its texture: the copper must have been raised in vapour and so deposited within its fibres. Gold has been found similarly studding the beams of refineries; and it may be seen to undergo volatilization in the focus of an intensely powerful burning glass. Fine wires of the most refractory metals may be dispersed in vapour by transmitting the discharge of a powerful Leyden battery through them.

(431) *Conducting Power for Heat and Electricity.*—The great differences of expansion exhibited by different metals, when exposed to equal degrees of temperature, have already been pointed out (126); and it may be stated generally that each metal possesses a specific expansion, and that the conducting power of each metal, both for heat (143), and for electricity is also definite (209 *bis*, 242); in general it is found that the best conductors of heat are also the best conductors of electricity: but though conductors in the solid and liquid conditions, the metals are insulators in the aeriform state.

(432) *Alloys.*—Metals enter into combination with each other, and form compounds termed ALLOYS, many of which are most extensively used in the arts. Comparatively few of the metals possess qualities such as render them suitable to be employed alone by the manufacturer; zinc, iron, copper, lead, tin, gold, silver, mercury, and platinum, constitute the entire number so used. Antimony, bismuth, and arsenic are too brittle to be used alone, but are employed for hardening other metals. Many of the physical properties of these metals are greatly altered by combination with others; the combination or alloy being often adapted to purposes for which either metal separately would be unfit. Copper alone is not fit for castings, and it is too tough to be conveniently wrought in the lathe or by the file; but when alloyed with zinc, it forms a much harder compound, which can be cast, rolled, or turned, and which constitutes the different kinds of brass, the qualities of

which can be varied by varying the proportions of the two metals. The addition of nickel to brass destroys its yellow colour, and produces the white compound metal known under the name of German silver. Copper and tin, in various proportions yield the hard, tough, but sufficiently fusible compounds known as bronze and bell metal. When the metals combine with mercury, the resulting body is called an *amalgam*.

In most cases these compounds of metals with each other are united by weak affinities; for it appears necessary in order to produce energetic union, that the substances when separate should exhibit great dissimilarity in properties. It has sometimes been questioned whether alloys are true chemical compounds: definite compounds of the metals with each other do however certainly exist, and some have been found combined in definite proportions in the native state. Such is the case with silver and mercury, which occur crystallized together in the proportion of 1 equivalent of silver to 2 of mercury; and that the alloys are undoubtedly in many instances true chemical compounds, is further shown by the increase or diminution in density which attends the act of combination; the specific gravity of the alloy being generally either above or below that of the two metals employed. Their fusing point is generally much lower than the mean of those of the metals which compose them. This circumstance, as well as the alteration which they exhibit in their general relations to heat and electricity, are also further evidences of the definite character of these compounds. A remarkable illustration of the influence which the chemical union of the metals exerts upon their fusing point, is afforded by the alloy called fusible metal, which is a mixture of single equivalents of bismuth, of lead, and of tin. They form a compound which melts at  $212^{\circ}$ , a temperature more than  $200^{\circ}$  F. below the fusing point of tin, the most fusible of these metals, and  $400^{\circ}$  below that of lead. Most frequently, however, the alloys are mixtures of definite compounds with an excess of one or other metal, and the separation of their components from each other is generally easily effected by simple means. Thus by exposing brass to a high temperature, the zinc volatilizes, leaving the copper behind; and from the alloy of arsenic and platinum, a heat sufficiently long continued will expel almost the whole of the arsenic. Even mere mechanical means will sometimes suffice. When silver, for example, is amalgamated with mercury, the amalgam formed is dissolved by an excess of mercury. This excess, however, may be almost entirely removed by squeezing the mass

through chamois leather; the amalgam is retained in the solid form, while the superfluous mercury, nearly freed from silver, escapes through the pores of the leather.

The ductility of metals is usually impaired by combination with one another. Alloys of two brittle metals are invariably brittle: such is the case with the compound of arsenic and bismuth. Alloys of a brittle with a malleable metal are also brittle. Even when two malleable metals are united, the compound is sometimes brittle. Gold, when alloyed with a minute portion of lead, splits under the hammer. Generally speaking, the hardness of metals is increased by alloying them; of this a familiar instance is afforded by the standard coin of the realm: both gold and silver, when unalloyed, are not sufficiently hard to resist attrition to the degree required for the currency, but the addition of  $\frac{1}{10}$ th or  $\frac{1}{12}$ th of their weight of copper to either metal increases its hardness to the requisite extent.

The more important alloys will, however, be best considered separately, when the individual metals which enter into their composition are described.

(433) *Condition in which the Metals occur in Nature.*—The ties which unite the components of an alloy are feeble and are easily severed; but the compounds formed by the metals with the class of substances known as non-metallic, are for the most part held together by affinities of a very powerful order, and these compounds are in a chemical point of view much more interesting and important than the alloys. With some of the metals, carbon and silicon combine in small proportion without appearing to destroy the metallic character; and, in fact, these compounds more resemble alloys than any other class of combinations: the most remarkable instances of carbides and silicides are furnished by iron, which, in its modifications of steel and cast iron, is combined with variable quantities of these elements. Many of the compounds of the metals with sulphur, preserve the metallic lustre, as is seen in galena and pyrites, yet lose nearly all other physical properties by which the metals are recognised; ductility, malleability, and power of conducting electricity are extremely impaired. The metallic character is still more completely destroyed by oxygen, which converts the metals into bodies apparently earthy, as in the familiar cases of lime, magnesia, alumina, and oxide of zinc: whilst chlorine and its allied group of elements form compounds which are most of them soluble, and possess all the qualities of true salts. The energy with which iron, zinc, and many other metals combine with



oxygen is very remarkable; and the affinities of chlorine are still more active.

The more common metals, on account of their powerful affinity for oxygen and sulphur, are very rarely met with in the uncombined form. Some of those which are less abundant are however found naturally in the metallic condition: such is the case with gold, silver, mercury, platinum, and (copper.) They are then said to occur in the *native state*. Many are found alloyed with each other: gold, for instance, forms native alloys with palladium and with silver; silver with mercury; antimony with arsenic. The occurrence of native metals or natural alloys is, however, an exceptional circumstance, as the majority of the metals are found in combination with other elements. Oxygen and sulphur, in particular, from their powerful affinities and the abundance in which they occur, are the bodies most frequently associated with them; at other times arsenic, and more rarely chlorine, are the mineralizing agents. These compounds, whether oxides, sulphides, arsenides, or chlorides, constitute what are termed the *ores* of the metals.

(434) *Distribution of the Metals*.—Next to silica in its various forms, the most abundant components of the rocks and superficial portions of the globe, are the compounds of lime, alumina, and magnesia. These earths are themselves oxides of metallic bodies, the affinity of which for oxygen is so intense that they are never isolated from it except for scientific purposes in the laboratory of the chemist. In their oxidized form they are everywhere scattered in abundance over the face of the globe. It is not so with those metals which man is in the habit of separating from their ores upon the large scale, and of employing for the various requirements of civilized society in the metallic state. Most of the ores of the highest importance and utility, constitute but a comparatively small portion of the components of the earth's crust; but this deficiency in their relative proportion is more than compensated by the mode of their distribution, for they are not dispersed at random, or diffused in minute quantity uniformly throughout the mass of the earth, but are collected in thin seams or beds, which form *mineral veins*.

Man has hitherto been able to penetrate but to a very small depth into the body of the earth, the deepest excavation which he has been enabled to make being not greater, in proportion to the diameter of the earth, than the thickness of an ordinary sheet of writing paper to a globe two feet in diameter. Geological observations have shown, and any person who has

traversed a railway cutting has had a partial opportunity of convincing himself of the fact, that the superficial portions of the globe which have hitherto been examined consist of a succession of beds or layers, *strata*, as they are commonly termed, which rest one above another: these beds in some places nearly retain their original horizontal direction; but usually they have assumed a position more or less inclined, so as to form a considerable angle with the surface. The same stratum is liable to great variations in thickness in different parts, but each bed is found to occur in a uniform position in the series, the successive strata following each other in regular order, the uppermost being those of most recent formation. In this way the London clay rests upon the chalk, the chalk upon what is termed the green sand, the green sand upon the gault, and so on. The stratified or *sedimentary* rocks rest upon others, which, like granite, porphyry, and basalt, show no appearance of stratification, but bear marks, more or less evident, of having undergone igneous fusion.

Occasionally it happens that a thin bed of metallic ore forms a part of the regular succession of the strata; thus in Staffordshire, over many square miles of country, thin bands or seams of the ore termed clay iron stone, varying in thickness from two to eight inches, are found lying between the beds of coal. Usually, however, the metalliferous masses occur in still older formations; such as in the mountain limestone of Cumberland and Derbyshire, or in the granite and clay slate, as in Cornwall; they are then found in fissures which traverse the ordinary strata of the district, and assume a direction which, though it never becomes quite vertical, still approaches more or less towards this position. These fissures vary in thickness from a few inches to as many feet; they are often filled with masses of basalt, granite, or trachyte (which have been injected from below, whilst the materials were in the molten state under the effects of subterranean heat), and then constitute what the miner terms *dykes*; but in other cases they are filled with metallic ores and form mineral veins, or *lodes*. The ore sometimes occurs nearly pure; at others mingled with quartz, fluorspar, and various crystallized minerals, or else with earthy impurities of different descriptions. These veins extend from the surface downwards often to a depth greater than can be followed even in the deepest mines. The veins which occur in the same district usually run in two directions, nearly at right angles to each other, the principal or original veins being traversed by the others. In Cornwall, for example, the metalliferous veins run

nearly east and west, but they are occasionally crossed more or less obliquely by other lodes, to which the term of *caunter* (contrary) *lodes* or *cross courses* has been given.

These cross courses, however, are by no means always metalliferous; they often appear to have been occasioned by the action of a force emanating from below, which, after bending and splitting the original strata, produced the fissures which were subsequently filled with quartz, clay, and various minerals. Such cross courses as these often occasion the miner much trouble and perplexity, since the subterranean force necessary to produce them is often attended with great displacement of the original strata. A valuable vein of ore is from this cause frequently interrupted, and is sometimes lost altogether for want of knowing in what direction to seek for it. This sudden break in a vein, and its displacement, in mining language is termed a *fault*. It is very rarely that a single mineral vein occurs alone; usually several are found together.

The thickness of the same vein, as might be expected, is subject to great variations; at one time it dwindles to a mere thread, at others it attains considerable expansion. The most productive veins usually occur near the junction of two dissimilar kinds of rock—the metallic ores having probably accumulated there in consequence of slow voltaic actions which have been going on through uncounted ages, and which have been occasioned by differences in chemical composition of the two contiguous rocks—in Cornwall, for example, where so large a proportion of the mineral wealth of Great Britain is accumulated, the most important mines occur upon the junction of the granite with the clay-slate or killas.

(435) *Mining Operations*.—The existence of a vein having been ascertained, and its dip and general direction having been determined, the miner commences by sinking a vertical pit, or *shaft*, in such a manner that he calculates upon cutting through the lode at some thirty or forty fathoms below the surface. When he has reached the lode, he *drives* a gallery, or *level*, horizontally into it, right and left, raising the ore to the surface through the shaft. If the produce be such as to encourage him to proceed, a second shaft is sunk in the course of the lode, at the distance of about 100 yards from the first, and into this the gallery or level is driven, so as to facilitate the ventilation of the mine and the extraction of the ore. In order to be able to remove the ore from other parts of the lode, above and below the point at which the first level is made, the shaft is continued downwards, and other galleries, or *cross cuts*, as they are termed, are made, both above

and below the first level, at intervals of ten fathoms, to meet the lode at different points; these cross cuts are at right angles to the levels. Fig. 283, shows a vertical cross section of the lode at the Callington Mine. *es* represents the engine shaft, *LL* the lode, and *cc* the cross cuts. The levels cannot be shown in this view; but whenever a cross cut meets the lode, a level is driven east and west, in the direction of the lode itself.

Fig. 284 shows the arrangement of the levels in the same mine; *es* represents the engine shaft, *w* a second smaller shaft,

FIG. 283.

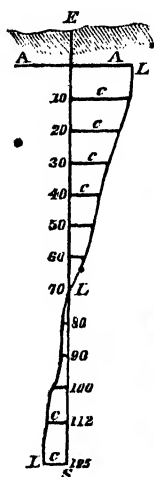


FIG. 284.

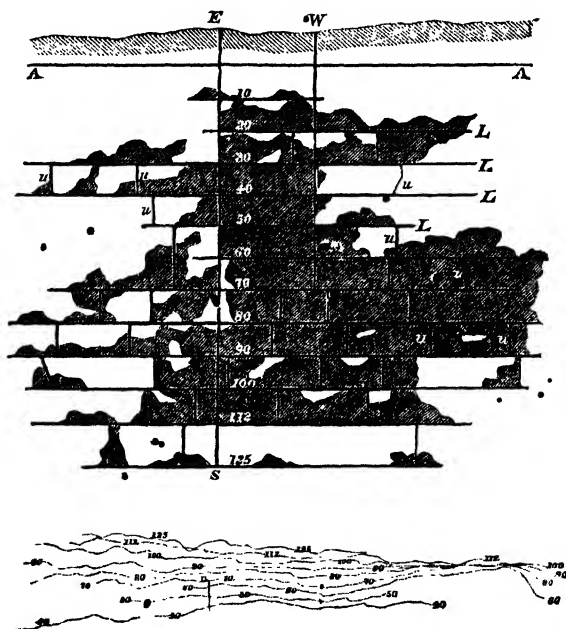


FIG. 285.

and *LL* the different levels, the depths of which in fathoms are indicated by the numbers attached to them; these levels communicate at different points by short cuts, or *winzes*, as the Cornish miners term them; they are shown at *uu*, in various parts, and are needed to facilitate the extraction of the ore from different points of the lode. The different levels are not immediately over, or parallel to each other, but their direction and position varies with that of the inclination and direction of the lode. This is explained by fig. 285, in which the direction of these galleries is exhibited; it

represents a *plan* of the mine, supposing the figures to refer to the levels shown in 284: the lode, it will be seen, does not preserve the same dip at all points, being much more nearly vertical at the right than at the left extremity of the plan. The cross cuts cannot be shown in fig. 284. The shaded parts in this figure indicate the portions of the lode which have been already worked away. The galleries in the mine are supported by strong timbering, the object of which is to prevent the rubbish from falling in and overwhelming the men while engaged in their work.

One of the principal difficulties which the miner has to contend with is the continual oozing of water into the mine in all directions. Where the mine, as very often happens, is situated upon the side of a hill, an *adit level*, or water course, shown at A A, fig. 284, is carried from the shaft to the lowest accessible point of the surface; and through this the waters of the upper part of the mine readily escape; but when the workings extend below this point, it becomes necessary to pump more or less constantly, and for this purpose powerful steam-engines are required. The galleries and levels are so constructed that the water shall flow from them into the principal shaft of the mine, so that by pumping from the *sump*, or lowest part of this shaft, the whole mine is freed from water. The greater part of the water is lifted only to the adit level, but a considerable quantity is raised to the surface for the purpose of washing the ore.

Much of the excavation is done by hand, with the pickaxe and wedges; but after judicious clearing, gunpowder properly applied facilitates the progress greatly. The quantities of powder used for blasting in the mines are small, usually about two ounces. The process of blasting consists in boring a hole to the depth of eighteen inches or two feet, somewhat obliquely, under the portion of rock which is to be raised; the powder is then introduced, and the hole is closed by ramming in clay or friable rock. A copper wire runs from the surface down to the charge, and when the ramming or *tamping* is finished, the wire is withdrawn and its place supplied with a pithed rush charged with powder, and the train is fired by means of a fusee. A safety fusee is now commonly substituted for the copper wire and pithed reed filled with powder. The ore that is detached is raised to the surface of the mine in large wrought-iron buckets, or *kibbles*, which are capable of containing about three hundred weight of ore.

(436) *Mechanical Treatment of the Ores.*—The extraction of metals from their ores is effected by two classes of operations:

those of the first class are mechanical; by their means the earthy parts contained in the matrix or vein-stone are to a certain extent separated: the operations of the second class are chemical, by which the metal itself is procured. The mechanical treatment is influenced not only by the nature and composition of the ore, but also by its market value: an ore of tin, copper, or lead, from the higher price which the metal bears, will be worth a more elaborate treatment than an ore of iron or zinc.

The ores of zinc and iron are occasionally subjected to the operation of washing: as when they are accompanied by a loose friable clay, the clay admits of being readily diffused in a finely divided state through the water, and is easily removed by its means. The specific gravity of clay being not much more than 2.0, whilst that of carbonate of iron and hydrated oxide of iron varies from 3.8 to 4.0, and calamine is about 4.2, these materials expose a smaller surface in proportion to their weight to the action of water than the clay, therefore when agitated with water they subside more rapidly; and if subjected to the action of a current of water, they are held for a shorter time in suspension, and are consequently carried by it to a smaller distance.

The same principles apply to the more elaborate processes of washing adopted with the ores of lead and tin. Galena has a specific gravity of 7.6; tinstone of about 7. Sulphate of baryta has a density of 4.6; fluorspar of 3.1; and quartz of 2.65. When reduced to particles tolerably uniform in size, the earthy portions may therefore be separated from the ores of lead and tin by the action of water to a considerable extent.

The following is an outline of the mechanical operations pursued in dressing the ores of lead and tin; and the same method is to a certain extent adopted with the copper ores:—

The ore having been brought to the surface, if a lead or copper ore, is first sorted by hand; the purest portions, or prills, as the Cornish miners term them, are set aside, and are ready for smelting without further preparation; but the bulk of the ore is broken by hammers into lumps about the size of a walnut, and the best pieces are again picked out by hand. The rougher portions go to the crushing mill, which consists of a pair of horizontal cylinders placed parallel to each other at a little distance apart: these cylinders may be either grooved or plain. The ore is supplied to them by a hopper from above. After passing through the mill, the crushed ore is sifted through coarse sieves; the coarser parts are set aside for the stampers, and the finer portion is subjected to the operation of

*jigging*. This consists in plunging the ore contained in a sieve into a pit, through which water is constantly flowing. The workman keeps the ore in continual agitation, alternately raising and lowering the sieve, to which he also gives an alternate rotatory motion, taking care always to keep it beneath the surface of the water. By this means the contents of the sieve are separated into layers of different quality. From its friable character, galena is easily reduced to small fragments: if it be a lead ore which is undergoing treatment, most of the galena, therefore, passes through the sieve and subsides to the bottom of the pit, whilst what is left upon the sieve consists chiefly of the less friable fluorspar and quartz. This residue is mixed with the inferior qualities of ore, and is transferred to the stamping mill, whilst the richer part is set aside for smelting.

Tin ore is usually disseminated through a compact hard matrix, and passes at once to the stampers.

The stamping mill consists of five or six upright wooden beams, the lower ends of which are shod with iron, each beam weighing about  $2\frac{1}{2}$  cwt. These are placed in a wooden frame, and are alternately lifted up and allowed to fall back upon the ore by the action of arms projecting from a horizontal axle, which is turned by water or steam power. The ore is placed on an inclined plane behind the stampers, and slides down under them, and is crushed. The crushed particles, when reduced to a sufficient degree of fineness, are washed out through a grating in front by the action of a current of water which is constantly flowing through the mill; the washed ore is carried into a channel in which two pits occur; in the one nearest the mill the purer and heavier part of the ore, or *crop*, is deposited; in the second the more finely divided portion, technically termed *slime*, or *schlich*.

The crushed ore now undergoes a series of washings, the object of which is to separate the impurities from the valuable part of the ore.

The crop is first subjected to washing in the *buddle*; this is a wooden trough, fig. 286, about eight feet long, three wide, and two deep, fixed in the ground, with one end somewhat elevated. At the upper end, a small stream of water enters, and is reduced to a uniform thin sheet by means of a distributing board, *a*, on which a number of small pieces of wood are fastened to break the stream. The ore to be washed is placed in small quantities at a time upon a board, *b*, somewhat more inclined than the body of the buddle, and it is spread out in a thin layer; the water carries it forward: the richer portions subside near the head of

the trough, and the lighter ones are carried further down. 'The heads' are then tossed in the *kieve* or tub, shown at *c*, which is filled with water, and ore added by a workman, who keeps the contents of the *kieve* in continual agitation by turning the paddle or agitator, the handle of which is seen projecting at top. When the vessel is nearly full, the agitation is stopped, and the *kieve* is struck smartly upon the side several times, and its contents

FIG. 286.



are allowed to subside; the upper half of the sediment is again passed through the buddle. Various modifications of the washing process are resorted to, but they are all the same in principle.

A rough estimate of the value of any sample of dressed ore is obtained by the process called *vanning*. A small quantity of the ore is placed on a shovel, and agitated gently with a peculiar circular movement in water, then by giving it a dexterous lateral shake, the different constituents arrange themselves according to their density—the galena, or the tin-stone, at bottom; above this are iron pyrites and blende; and at the top are the fluor and quartz. The eye then at a glance roughly estimates the quantity of each.

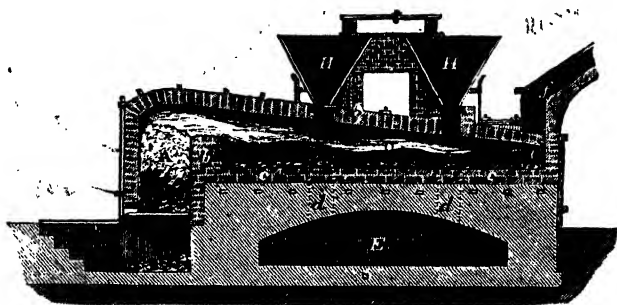
The water employed in the various washings is not allowed at once to run to waste, but is made to pass through a long shallow channel, in which the slime and mud which have been carried away in the different operations may subside. This slime still retains some portion of ore; and in order to recover this as far as possible, it is again subjected to the action of a fine stream of water, either upon an inclined table, which acts in a manner similar to the buddle, or it is washed upon a swinging table, the bed of which is also inclined, but moveable, and is suspended by chains from supports at the four corners; it is alternately thrust forward two or three inches by the revolution of a cam wheel, and is then allowed to fall back against solid wooden bearings with a sudden jar. The ore is spread upon a board which overhangs the upper



part of this table, and carried forward by a gentle stream of water; the heavier particles of the ore, owing to the superior momentum which their density gives them, are by this jarring movement of the board carried back to the upper part of the table, whilst the lighter impurities are washed away.

(437) Roasting, or Oxidation.—The chemical operations are divisible into two main branches, one dependent on the addition, the other on the removal, of oxygen. If the mineral contain volatile ingredients, such as sulphur or arsenic, the process of roasting, or oxidation, is first resorted to. In principle it is very simple; the mode of effecting it varies, however, in different cases. In the most common method, a furnace of particular construction, termed a *reverberatory*, is employed. Fig. 287 shows a section of a reverberatory furnace, such as is employed for roasting copper ores; *t* is the platform, from which the hoppers, *h h*, are charged with the ore, which at proper intervals is allowed to fall upon the bed, *c c*: the fuel is consumed upon a distinct hearth, *A*, and does not come into contact with the ore, from which it is separated by the bridge, *b*: the heated gases, as they arise from the burning mass, are, from the construction of the arched roof,

FIG. 287.



reverberated, or driven down upon the ore to be roasted, and then pass off through the flue, *f*: when sufficiently roasted the ore is allowed to fall into the arched recess, *E*, beneath the bed of the furnace through openings, *d d*, which are kept closed by sliding plates till the roasting is complete. After the fire has been lighted, a constant supply of air to the mineral is maintained, and care is taken to prevent the heat from rising so high as to melt the ore, which is stirred at intervals to expose fresh surfaces to the action of the air; the sulphur burns off in the shape of sulphurous acid, which escapes into the atmosphere; whilst the arsenic forms arsenious

acid, which, though volatile, speedily condenses, and is collected on the sides of the chimney, or else in chambers constructed for its reception, whence it is removed at intervals, and subsequently purified.

(438) *Reduction or (Smelting).*—The mass which remains after the volatile matters have been burned off, generally becomes oxidized from the continual supply of air at a high temperature. This oxidized mass then requires treatment by the second chemical process, that of *reduction*, which is applicable to most metallic oxides, whether of natural or of artificial origin. The object now is to remove the oxygen, by presenting to the mineral some body which, at a high temperature, has a stronger affinity for oxygen than the metal itself possesses. Furnaces of great size, varying in form with the nature of the metal, are employed in this operation. In them the ore is heated intensely, in contact with carbon. Carbonic oxide and carbonic acid are thus produced, and from their gaseous nature are instantly removed from the sphere of action. It becomes necessary at this stage to get rid completely of the earthy and other impurities of the ore, which the mechanical operations never succeed in removing entirely, and which often form a large proportion of the ore. In order to effect this, certain fluxes, or substances which are capable of forming fusible compounds with the earthy matters, are added at the same time with the carbon; these melt and form a kind of glass through which the reduced metal, from its superior density, sinks, and is thus completely defended from contact with the air: the metal is at suitable intervals drawn off from the bottom of the furnace; while the melted glass, or *slag*, as it is termed, runs off at an aperture left in the side for the purpose. Limestone is in some cases added to the ore with the view of aiding the fusion of the siliceous impurities; in other instances fluorspar or some other readily fusible material is added, for the purpose of increasing the fluidity of the slag. Much judgment is required in the selection of the flux, and in deciding upon the proper proportion to be added: frequently this object is economically effected by a judicious mixture of different ores of the same metal, each of which aids the other by supplying some compound which was wanting to render the slag sufficiently fusible.

The various modifications of these processes will be described as they present themselves in connexion with the different metals which require these modifications. Other modes of separating individual metals are employed, which will be alluded to in their

respective places. For details upon metallurgic processes, the fourth volume of Dumas' valuable work, *Traité de Chimie appliquée aux Arts*, may be consulted; and the second and third volumes of the same work contain many excellent descriptions of processes in which metallic chemistry is applied to the purposes of industry and commerce. Phillips's *Metallurgy* is a smaller and more compendious treatise upon this subject.

(439) *Classification of the Metals*.—For the convenience of description the metals may be divided into seven groups (page 437):

I. The metals of the alkalis; these are three in number—viz.,

1. Potassium
2. Sodium
3. Lithium.

With them will be described the salts of oxide of ammonium; they are isomorphous with the potash salts, and indeed present the closest analogy with them.

The metals of the alkalis are distinguished by the following characters:—They have an intense affinity for oxygen, and become tarnished immediately that they are exposed to the air: when thrown upon water, they decompose it at all temperatures with rapid disengagement of hydrogen: their oxides combine with water with great avidity, and dissolve in it, forming solutions which are powerfully caustic and alkaline. In these oxides the basic quality, or their capacity for saturating the acids, is developed to the highest degree. The alkalis, when exposed to the air, either in the solid form or in solution, rapidly absorb carbonic acid. Each alkali forms with this acid two salts, a carbonate and a bicarbonate, both of which are freely soluble in water. The metals of the alkalis combine with sulphur in several proportions; all of these compounds, also, are soluble. With chlorine they form but a single chloride; but their oxides have the power of combining with chlorine, and forming compounds possessed of bleaching properties. Lithium, from the sparing solubility of its carbonate, forms the connecting link between this group and the one which follows it.

II. The metals of the alkaline earths are four in number—viz.,

1. Barium
2. Strontium
3. Calcium
4. Magnesium.

These metals, with the exception of magnesium, decompose water at all temperatures with great rapidity. They form but one oxide, which is soluble to a certain extent in water, and which is capable of combining with acids; they form several sulphides which are

soluble in water; the protosulphides being less so than those which contain higher proportions of sulphur. With chlorine their oxides form bleaching compounds. Their carbonates are insoluble in pure water, but dissolve to a small extent in water charged with carbonic acid. Magnesium, from its power of resisting oxidation, the isomorphism of its oxide with protoxide of zinc, the sparing solubility of its sulphide, the solubility of its sulphate, and several other particulars, forms the connexion between this and the fourth group.

### III. Metals of the earths; ten in number:—viz.,

- |              |            |               |
|--------------|------------|---------------|
| 1. Aluminum  | 5. Yttrium | 8. Cerium     |
| 2. Glucinum  | 6. Erbium  | 9. Lanthanium |
| 3. Zirconium | 7. Terbium | 10. Didymium. |
| 4. Thorium   |            |               |

The oxides of this class are insoluble in water, but they dissolve either in the caustic alkalies or in their carbonates. Aluminum and glucinum do not decompose water unless the metals are in a very finely divided state; the other metals of this group are scarcely known in an isolated form. The basic character of the oxides of this group of metals is much less marked than that of the preceding groups. Many of these metals are very rare, and their properties have been but imperfectly examined. Aluminum, by the isomorphism of its oxide with sesquioxide of iron, the volatility of its chloride, its slight affinity for carbonic acid, and other peculiarities, connects this group with the one which follows.

IV. METALS MORE OR LESS VOLATILE IN VAPOR, EIGHT IN NUMBER:—viz.,

- |            |            |               |
|------------|------------|---------------|
| 1. Zinc    | 4. Nickel  | 7. Chromium   |
| 2. Cadmium | 5. Uranium | 8. Manganese. |
| 3. Cobalt  | 6. Iron    |               |

These metals, when heated to dull redness, decompose the vapour of water if it be transmitted over them; they become converted into oxides, whilst hydrogen escapes; they also dissolve with effervescence and evolution of hydrogen in dilute sulphuric or in hydrochloric acid. The protoxides of these metals are powerful bases; all of these protoxides dissolve more or less freely in ammonia, especially if chloride of ammonium be present in the solution. Several of the metals of this group—viz., iron, chromium, and manganese, form powerful metallic acids, when combined with three or more equivalents of oxygen, and the acids thus formed are very soluble in water. Hydrated sulphides of these metals are produced by the addition of solution of sulphide of potassium or of ammo-

nium to solution of their salts; the precipitate so occasioned is insoluble in excess of the alkaline sulphide. The salts of sesquioxide of chromium, however, are precipitated as oxide of chromium, not as sulphide. Sulphuretted hydrogen gas, when transmitted through the solutions of these metals acidulated with sulphuric acid, occasions no precipitate of sulphide excepting in the case of the salts of cadmium.

V. Metals which yield powerful acids with oxygen; of these there are eleven, as follow:—viz.,

- |              |               |                |
|--------------|---------------|----------------|
| 1. Tin       | 5. Ilmenium   | 9. Antimony    |
| 2. Titanium  | 6. Molybdenum | 10. Arsenic    |
| 3. Columbium | 7. Tungsten   | 11. Tellurium. |
| 4. Niobium   | 8. Vanadium   |                |

The metals which belong to this class decompose water when its vapour is driven over them at a red heat, (with the exception of arsenic and tellurium, which are more allied in character to phosphorus and sulphur than to the metals,) but they do not evolve hydrogen when treated with dilute sulphuric acid, owing to the want of basic power in their oxides.

Protoxide of tin is a powerful base, and this metal forms the transition from the group of the iron metals to the present group. The metallic acids formed by these metals are, with the exception of arsenic acid, nearly insoluble in water. The sulphides of this group of metals are soluble in the alkaline sulphides, and form in many cases crystallizable compounds with them.

VI. The next group contains but three metals:

1. Bismuth      2. Copper      3. Lead.

They exert no decomposing action upon water, even at a full red heat; they form powerful basic oxides, and exhibit a strong tendency to the formation of subsalts. Bismuth exhibits a certain analogy with antimony. Copper forms salts which are isomorphous with those of the protoxides of the metals in the iron group, and in the compounds which it forms with carbonic acid, displays a close correspondence with magnesia, zinc, cobalt, and nickel; and lead in some of its compounds is isomorphous with those of the alkaline earths. The three metals which compose this group, are not dissolved by either dilute sulphuric or hydrochloric acid; they are precipitated from acid solutions by sulphuretted hydrogen, and their sulphides do not combine with the sulphides of the alkaline metals.

VII. The last group consists of the noble metals, of which there are nine—viz.,

- |            |              |              |
|------------|--------------|--------------|
| 1. Mercury | 4. Platinum  | 7. Ruthenium |
| 2. Silver  | 5. Palladium | 8. Osmium    |
| 3. Gold    | 6. Rhodium   | 9. Iridium.  |

These metals are unable to decompose water at any temperature. They have so feeble an affinity for oxygen that their oxides, with the exception of those of osmium, are decomposed below a red heat, the metal remaining in an uncombined form. In many cases simple exposure to a strong light produces a similar decomposition. All of them yield more than one oxide capable of forming salts. Mercury and silver are often found as sulphides, but the others usually occur in the native state, several of them being frequently associated together. Their affinity for sulphur and for chlorine is much stronger than for oxygen. All of them form at least two chlorides, and some three or even four. The chlorides of the noble metals have a strong tendency to form double chlorides with the chlorides of the metals of the alkalies.

Silver exhibits considerable analogy with lead; its oxide possesses very strong basic power; palladium is closely allied to copper.

## § II. GENERAL PROPERTIES OF THE COMPOUNDS OF THE METALS WITH THE NON-METALLIC ELEMENTS.

(440) THE OXIDES.—The most important compounds of the metals with the non-metallic bodies are those which they form with oxygen. The oxides in many cases form abundant and valuable metallic ores; such as the different forms of hæmatite, the specular and magnetic iron ores, and tinstone, the ordinary ore of tin.

The oxides in general are devoid of all metallic appearance, and present *par excellence* the characters of earthy matters. The protoxides, when solid, are all insulators of the voltaic current. Some of the higher oxides, as the binoxides of silver, lead, and manganese, allow it to pass with almost as much facility as a metal itself would do. It is singular that all these conducting peroxides may be formed in solutions by the action of the current itself.

The oxides, when found crystallized in the native state, are much harder than the metals that furnish them, and they generally have a specific gravity considerably less than the metals themselves. All the oxides at ordinary temperatures are solid; many fuse at a

red heat, as the protoxides of potassium, sodium, lead, and the sesquioxide of bismuth: the oxide of copper, molybdic acid, sesquioxide of chrome, and black oxide of iron, require a much higher temperature to effect their fusion. Baryta, strontia, and alumina require the heat of the oxyhydrogen jet, while upon some, such as lime and yttria, no appearance of fusion is exhibited, even after the application of the most intense heat.

As a general rule, the addition of oxygen to a metal renders it much less fusible and volatile. The protoxide of iron, the sesquioxide of chrome, and molybdic acid, are the only oxides which melt at a temperature below that of the metal from which they are produced. A few of the oxides are volatile at moderate temperatures; among these are arsenious acid, sesquioxide of antimony, and tassaroxide of osmium. Six only of the basic oxides are soluble—viz., the three alkalis, and baryta, strontia, and lime. The insolubility of the oxides, however, is far from being so complete in general as that of the corresponding sulphides, and consequently, except in particular cases, it is less advisable in analytical operations to separate the metals in the form of oxides than in that of sulphides.

Those compounds of oxygen with the metals which possess acid characters are often freely soluble in water, as, for example, the chromic, manganic, and arsenic acids; others, as the molybdic and tungstic acids, are more sparingly taken up; but even those acids which, like the tantallic and telluric, are insoluble, form hydrates which usually redden litmus paper.

By the action of a red heat many of the oxides lose their oxygen, either partially or entirely. The oxides of the noble metals are completely reduced; the peroxides of lead, of cobalt, of nickel, and of barium return to the state of protoxide; and arsenic and chromic acids are converted respectively into arsenious acid and sesquioxide of chromium. It may be stated as a general rule, liable however to exception, especially in the case of the acidifiable metals in the fifth class, that the affinity of a metal for oxygen increases in the inverse proportion of its specific gravity; the lightest metals, such as potassium and sodium, being the most readily oxidized, while platinum, iridium, and gold, which are the densest metals, are also those which show the smallest tendency to combine with oxygen.

The compounds of the same metal with oxygen are often numerous; and the extremes, or the oxide with the maximum of oxygen and the oxide with the minimum of oxygen, frequently present

chemical qualities of opposite kinds, the former being electro-negative, and possessing acid properties, whilst the lower oxides are electro-positive, or basic in their nature.

An excellent instance of this kind is afforded in the various oxides of manganese: the protoxide, ( $\text{MnO}$ ), is a powerful base, the sesquioxide, ( $\text{Mn}_2\text{O}_3$ ), is a much weaker base; the deutoxide, ( $\text{MnO}_2$ ), enters into combination neither with acids nor alkalies, while the two higher oxides, manganic and permanganic acids, ( $\text{MnO}_3$ ) and ( $\text{Mn}_2\text{O}_7$ ), combine with alkalies, and are true acids. As a general rule, the greater the number of equivalents of oxygen which an oxide contains, the less is it disposed to unite with the acids: on the contrary, it frequently possesses acid properties, and then it unites with bases to form salts. Protoxides generally are strong salifiable bases; to form neutral salts, they require 1 equivalent of acid. Sesquioxides are weaker bases; their salts are usually unstable; they require 3 equivalents of acid to form a salt which is neutral in composition, and in general all oxides require as many equivalents of acid as they contain equivalents of oxygen in their composition.

*Preparation of the Oxides.*—Most of the oxides may be procured in combination with water; generally speaking, these hydrated oxides are obtained by double decomposition, on the addition of an alkali to one of their soluble salts: thus sulphate of zinc yields hydrated oxide of the metal on adding hydrate of potash to its solution;  $\text{ZnO}, \text{SO}_3 + \text{KO}, \text{HO} = \text{KO}, \text{SO}_3 + \text{ZnO}, \text{HO}$ . The metals which form powerful bases, like those of the alkalies and alkaline earths, retain the water with great obstinacy; while others, which are less powerful bases, such as the hydrated oxide of copper, are decomposed at a temperature below that of boiling water.

The anhydrous oxides may be obtained in several ways:—

1. They may often be formed directly, by burning the metal in air, or in oxygen gas. This process is best adapted to metals which, like zinc or arsenic, are volatile, or which produce fusible oxides, like iron or lead; in such cases the oxide is removed as fast as it is formed, and fresh surfaces of the metal are continually exposed to the action of the gas. Anhydrous potash and soda cannot be obtained by any other method; and it is resorted to, on the large scale in the preparation of arsenious acid, and of the oxides of zinc and lead. Several of the metallic protoxides, if roasted at a low red heat in a current of air or of oxygen, absorb an additional quantity of oxygen. Litharge, or protoxide of lead, is thus converted into red lead,  $2 \text{PbO}, \text{PbO}_2$ ; and peroxide of barium,  $\text{BaO}_2$ ,



may in this way be obtained from baryta. 2. Another method consists in the formation of a nitrate of the oxide of the metal by means of nitric acid; the nitrate is then decomposed by heat, which expels the acid and leaves the oxide: in this way the oxides of mercury, bismuth, antimony, copper, barium, and strontium are prepared. 3. In some cases it is found advantageous to prepare the oxide by the decomposition of the carbonate of the metal by heat. All the carbonates, with the exception of those of soda, potash, and baryta, are decomposed at a red heat. Lime is thus commonly obtained from limestone, which is an impure carbonate. 4. Sometimes the hydrated oxide is precipitated, as already mentioned, and then rendered anhydrous by heat; in this manner sesquioxides of iron and uranium are often prepared. 5. All the acid oxides may be obtained by deflagrating the metal or its sulphide with nitrate of potash; the tendency of the metallic acid to unite with the alkali favours the oxidation of the metal: the higher oxides of osmium, of titanium, and of chromium and others may be obtained in this way.

*Decompositions.*—The oxides are not affected by hydrogen gas at the ordinary temperature of the air. All the higher oxides of the metals are readily reduced to protoxides by hydrogen at a low red heat, whilst water is formed; and at a full red heat a large number of them are reduced to the metallic state. This reduction goes on most readily when the current of hydrogen is brisk, so that the vapour of water is carried away as fast as it is formed. The oxides of many of the metals which decompose water at a red heat may nevertheless be deprived of their oxygen in a current of hydrogen; this is the case, for example, with the oxides of iron, of zinc, and of cadmium. The metals of the alkalies and of the earths are not reducible by hydrogen.

The reducing action of carbon at a high temperature is still more important; all the metals which yield their oxygen to hydrogen do so to carbon, and potassium and sodium are obtainable from their compounds by its agency. This arises in part from the volatility of these two metals, which is sufficient to enable them to be distilled from the carbonaceous mixture. Lithium and the metals of the earths are not volatile, and though their affinity for oxygen is less intense than that of potassium or of sodium, they cannot be obtained from their oxides by the action of carbon. It depends upon the nature of the metal, and upon the temperature employed, whether the gas that is formed during the reduction be carbonic oxide or carbonic acid. The more readily-oxidizable metals, such

as potassium, zinc, and iron, at a high temperature decompose carbonic acid, so that carbonic oxide only is formed when they are reduced; while if the reduction take place readily, as is the case with copper and lead, carbonic acid is produced.

Dry chlorine sometimes, even without the application of heat, decomposes the basic metallic oxides, expelling their oxygen, and converting them into chlorides. At an elevated temperature few of them, excepting those of magnesium and of the earths in the third group, resist its action; the oxides of gold and platinum are simply reduced to the metallic state; but chlorides are formed in other cases.

If the oxides be hydrated and suspended in water, the action of chlorine is quite different; the metals of the first two groups yield bleaching compounds, and by heat are converted into chlorates and chlorides in the manner already explained (321). The oxides of the third group experience no particular change, but those in the fourth group are converted into a mixture of chloride and sesquioxide. The sesquioxides of cobalt and of nickel are usually prepared in this manner: thus,  $3 \text{CoO} + \text{Cl} = \text{CoCl} + \text{Co}_2\text{O}_3$ .

If the liquid be strongly alkaline, the whole of the metal may be converted into sesquioxide;  $2 \text{CoO} + \text{KO} + \text{Cl} = \text{Co}_2\text{O}_3 + \text{KCl}$ . The potash in this case parts with its oxygen, which is transferred to the cobalt, whilst the chlorine combines with the potassium. The protoxide of manganese under these circumstances yields the hydrated peroxide, ( $\text{MnO}_2$ ).

If the metal be capable of forming an acid with 3 equivalents of oxygen, the process of oxidation may proceed further, and the sesquioxide may, in the presence of a large quantity of potash, become converted into the metallic acid, which combines with a portion of the excess of alkali; thus in the case of peroxide of iron,  $\text{Fe}_2\text{O}_3 + 5 \text{KO} + 3 \text{Cl} = 2(\text{KO}, \text{FeO}_3) + 3 \text{KCl}$ ; ferrate of potash being produced.

Most of the oxides are decomposed more or less completely when heated with sulphur; the alkalis and alkaline earths are converted into sulphates and sulphides, but the metals of the earths, or those of the third group, are unaltered. Most of the other oxides are converted into sulphides with escape of sulphurous acid. The oxides are more readily decomposed by sulphur if they be previously mixed with carbon.

(441) *Estimation of Oxygen in Metallic Oxides.*—The composition of a metallic oxide may be ascertained, if it be decomposable by hydrogen, by heating the compound in a current of this gas

and collecting and weighing the water produced, and determining the amount of reduced metal which a given weight of the oxide has yielded. In other cases a given weight of the metal is converted into oxide, either by heating the metal in a current of air, or by converting it into a nitrate, and afterwards expelling the nitric acid by the application of heat, and weighing the quantity of oxide which is left.

(442) **SULPHIDES.**—The combinations of sulphur with the metals are numerous, and in many instances of great value. A large number of them occur as natural productions, in which case they often exhibit a high metallic lustre; as is shown by the sulphides of iron, copper, lead, and antimony.

Sulphur often combines with the same metal in several proportions, and it usually happens that for each oxide a corresponding sulphide may be formed. It sometimes happens, as in the case of the metals of the alkalies and alkaline earths, that the sulphides are more numerous than the oxides: thus two oxides of potassium, sodium, and barium only are known, but there are not fewer than five sulphides of these metals.

All the metallic sulphides are solid at ordinary temperatures. Most of them fuse at a heat a little above redness, and if the air be excluded, the protosulphides undergo no change; the higher sulphides, as the bisulphide of iron and bisulphide of tin, are decomposed, and give off the second equivalent of sulphur, whilst a protosulphide of the metal is left. Tersulphide of arsenic, or orpiment,  $\text{As}_2\text{S}_3$ , and sulphide of mercury, or cinnabar,  $(\text{HgS})$ , may even be sublimed; that is to say, they may be converted into vapour, and re-condensed in the solid form. Indeed, these sulphides are usually purified by this operation.

If the air be allowed free access to the heated sulphides, they are all decomposed; the sulphur becomes oxidized, and passes off as sulphurous acid, whilst the metal in most cases remains in combination with oxygen. The sulphides of the alkaline metals and of the earths become converted into sulphates of the base, and the same thing occurs less completely with many of the metals which have a strong affinity for oxygen; the sulphides of iron, lead, and copper are partially converted into sulphates, but by a stronger heat these sulphates lose their acid, and the oxide of the metal only is left. The sulphides of the noble metals, when roasted in a current of air, lose their sulphur, which burns off in the form of sulphurous acid, while the pure metal remains behind.

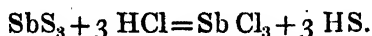
The sulphides are all insoluble in water, with the exception of those of potassium, sodium, calcium, strontium, and barium. Sulphide of magnesium is sparingly soluble.

The sulphides, like the oxides, may be subdivided into basic and acid sulphides, according to the nature of the metal, and the number of equivalents of sulphur with which it is combined. The protosulphides of the alkaline metals afford illustrations of basic sulphides, and they enter into combination with the higher sulphides of metals which, like antimony and arsenic, form acids with oxygen. Pentasulphide of arsenic, or sulpharsenic acid, in this way combines with sulphide of sodium, and forms a crystalline soluble compound,  $(3 \text{ NaS}, \text{AsS}_5 + 15 \text{ aq})$ , and in like manner pentasulphide of antimony, or sulphantimonic acid, forms a soluble compound with sulphide of sodium,  $(3 \text{ NaS}, \text{SbS}_5 + 18 \text{ aq})$ , which crystallizes in beautiful transparent tetrahedra. A large number of similar compounds may be formed with the sulphides of other metals, and these compounds are for the most part soluble in water.

In consequence of the tendency to the formation of these double sulphur salts, many of the sulphides which are insoluble in water dissolve freely in solutions of sulphide of potassium or sulphide of ammonium; and this circumstance is frequently taken advantage of in the laboratory during the progress of an analysis, for the purpose of separating certain metals which are soluble in the alkaline sulphides from others which are not soluble. The following sulphides dissolve in a solution of hydrosulphate of ammonia, and in solution of sulphide of potassium:—

Tersulphide of gold . . . $\text{AuS}_3$	Tersulphide of tungsten . . . $\text{WS}_3$
Bisulphide of platinum . . . $\text{PtS}_2$	Tersulphide of molybdenum . . . $\text{MoS}_3$
Sesquisulphide of rhodium . . . $\text{Ro}_2\text{S}_3$	Quadrisulphide of molybdenum . . . $\text{MoS}_4$
Tersulphide of arsenic . . . $\text{AsS}_3$	Protosulphide of tin . . . . . $\text{SnS}$
Pentasulphide of arsenic . . . $\text{AsS}_5$	Bisulphide of tin . . . . . $\text{SnS}_2$
Tersulphide of antimony . . . $\text{SbS}_3$	Bisulphide of tellurium . . . $\text{TeS}_2$
Pentasulphide of antimony . . . $\text{SbS}_5$	Tersulphide of tellurium . . . $\text{TeS}_3$
Bisulphide of vanadium . . . $\text{VS}_2$	The sulphides of iridium.
Tersulphide of vanadium . . . $\text{VS}_3$	

A large number of the sulphides, especially those of the more oxidizable metals, dissolve in hydrochloric acid when cold, and still more readily when heated; a chloride of the metal and hydrosulphuric acid being formed. It is in this way that hydrochloric acid acts upon the tersulphide of antimony;



Sulphuric acid, when dilute, acts in a similar manner upon the

sulphides of the more oxidizable metals, though less readily than hydrochloric acid. The sulphides are all decomposed when heated in a current of chlorine gas, chloride of sulphur and chloride of the metal being formed. This property is sometimes made use of in the analysis of ores consisting chiefly of sulphides, or of sulphides and arsenides of the metals; the volatile metallic chlorides are in this way separated from the more fixed ones. Aqua regia attacks and decomposes the sulphides as readily as gaseous chlorine. Most of them are also decomposed by nitric acid, sulphuric acid and nitrate of the metal being formed; part of the sulphur often separates in the form of tough elastic masses, which, if the heat be continued, collect into yellow globules, and can be oxidized only by prolonged digestion in the acid.

Before the blowpipe, the sulphides are easily recognised by the odour of sulphurous acid which they emit, either when heated in a glass tube open at both ends, or when roasted upon charcoal. Some other particulars relating to the sulphides have been already mentioned (356).

*Preparation.*—Many methods for preparing the sulphides may be adopted. 1. Sulphur may be heated with the metallic oxides, many of which it decomposes: with the alkalis and the alkaline earths, a sulphate, and a sulphide with variable proportions of sulphur, are obtained: but when definite and pure sulphides are required, other means should be adopted. 2. The protosulphides of the metals of the alkalis and of the alkaline earths may be procured by decomposing the sulphates of these metals by igniting them with charcoal; oxygen is removed, carbonic oxide formed, and the remaining sulphide may be dissolved in water and freed from the excess of charcoal;  $\text{KO}, \text{SO}_3 + 4\text{C} = \text{KS} + 4\text{CO}$ . 3. Hydrogen is sometimes employed for preparing the sulphides from the sulphates, which are to be placed in a tube and ignited in a current of the gas. In this manner the alkaline protosulphides are easily obtained: the sulphates of the other metals frequently lose a portion of sulphur, as well as all their oxygen, and subsulphides are procured. 4. Sulphides of the metals may also be procured, with the exception of those of the four first groups, by passing a stream of sulphuretted hydrogen through neutral or acid solutions of their salts, when they are precipitated, often with peculiar and characteristic colours. 5. The hydrated sulphides of zinc, iron, manganese, cobalt, and nickel, which are not thrown down by sulphuretted hydrogen, may be prepared by double decomposition, by mixing a solution of the salts of any of these metals with that of an alkaline sulphide: thus

sulphate of manganese if mixed with sulphide of potassium yields sulphate of potash and sulphide of manganese;  $\text{MnO}, \text{SO}_3 + \text{HO}, \text{KS} = \text{KO}, \text{SO}_3 + \text{HO}, \text{MnS}$ . 6. Many of the metals combine directly with sulphur, if heated with it, and form sulphides; the compounds thus obtained often contain sulphur dissolved in, or disseminated through, the mass. Sulphide of iron is usually prepared in this manner. Indeed, sulphur, though itself combustible, supports the combustion of many metallic bodies, which burn vividly when heated in its vapour.\*

(443) *Estimation of Sulphur in Metallic Sulphides*.—Sulphur is always estimated either in the form of sulphuric acid or of free sulphur. Sulphur is easily converted into sulphuric acid by the agency either of gaseous chlorine or of aqua regia, and the soluble sulphates, when mixed in an acid solution with a salt of baryta, yield an insoluble sulphate of baryta, which, when well washed with boiling water and ignited, furnishes data for the calculation of the sulphur; 100 parts of sulphate of baryta contain 34.32 of sulphuric acid, or 13.73 of sulphur. If a salt of silver be present, nitrate of baryta must be employed to precipitate the sulphuric acid.

If during the solution of a sulphide in aqua regia, the sulphur have collected into clear yellow fumes, and the action upon the ore appears to be complete, it is not necessary to wait till the whole of the sulphur is dissolved: the undissolved portion may be collected on a small counterpoised filter, and weighed, and its amount must be added to that which has been converted into sulphuric acid; the proportion of which is to be ascertained by means of a baryta salt in the manner above described.

(444) **CHLORIDES**.—In colour and external appearance the metallic chlorides exhibit considerable variety. They are all fusible at moderate temperatures, and melt much more readily than the corresponding oxides. Many of them are semi-transparent after fusion: in general they are sectile compounds, and possess but an inferior degree of hardness. In the solid form the chlorides are non-conductors of electricity, but the protochlorides, when fused, transmit the voltaic current, and experience decomposition. The action of chlorine upon the metals is generally stronger than that of oxygen upon them; but if a metallic chloride be heated in a current of oxygen or of atmospheric air, the chlorine is expelled, and an oxide of the metal is produced. The only instances in which this decomposition does not take place, occur in the case of the chlorides of the noble metals and in those belonging to the

first and second groups. Chloride of magnesium is however readily decomposed in this manner.

In the case of the metals which have but slight affinity for oxygen the chlorides generally correspond in number with the oxides; and for every chloride an analogous oxide is always obtainable; but when the metal exhibits a strong affinity for oxygen, and forms a powerful base, the number of oxides frequently exceeds that of the chlorides. When mixed with water, the chlorides of some of the acidifiable metals are decomposed. In such cases it sometimes happens that hydrochloric acid and the metallic acid are formed, as occurs when chloride of tungsten or the perchloride of antimony are diluted;  $\text{SbCl}_5 + 5 \text{HO} = \text{SbO}_5 + 5 \text{HCl}$ . In other cases, the chloride is only partially decomposed, and a portion of it unites with the newly formed oxide, thus producing an oxychloride of the metal, whilst hydrochloric acid is set free. Terchloride of antimony and chloride of bismuth furnish instances of this kind: thus,  $3 \text{BiCl}_3 + 9 \text{HO} = \text{BiCl}_3 + 2 (\text{BiO}_3, 3 \text{HO}) + 6 \text{HCl}$ . From these cases it has been argued by some chemists that all chlorides, when put into water, decompose that liquid, and that when they remain dissolved a hydrochlorate of the oxide is formed. There are strong reasons, however, for doubting the general applicability of this view: it is found, for instance, that in many cases, on crystallization, the anhydrous chloride separates from the aqueous solution, as occurs with copper salt.

*Formation.*—1. Many of the metallic chlorides may be formed by heating the metal in a current of dry chlorine: in this way the perchlorides of antimony and of iron are procured. 2. An easier method, in cases where it is applicable, consists in dissolving the oxide or the carbonate of the metal in hydrochloric acid, and evaporating the solution to dryness, or till crystallization commences. Chlorides of cobalt, of nickel, and of calcium may be thus obtained. This process, however, fails in many cases, particularly in the class to which the earths belong; chlorides of magnesium and aluminum, for example, lose their chlorine when their solutions are evaporated in contact with the air or with oxygen. 3. In cases where the chloride is volatile, like those of aluminum and glucinum, the oxide of the metal is mixed with charcoal, and a current of dry chlorine is transmitted over the mixture; the charcoal removes the oxygen as carbonic oxide, and the chlorine, uniting with the metal, forms a chloride which volatilizes and condenses in the cool part of the apparatus. If the basic oxides be heated to redness in a current of

dry chlorine, oxygen is expelled and a chloride of the metal remains; but this process is never adopted for procuring the chlorides.

Many of the chlorides of the more electro-negative metals are decomposed when heated with the more electro-positive metals. Bichloride of tin may thus be obtained by heating metallic tin with an excess of corrosive sublimate; and the tetrachlorides of antimony and of bismuth may be obtained in a similar manner. Sometimes this process is employed for the purpose of isolating those metals the oxides of which resist decomposition by the usual means. In this way sodium is employed to decompose the chloride of aluminum or of magnesium for the purpose of procuring the aluminum or magnesium in an uncombined form; and in a similar manner potassium is employed to decompose the protochloride of uranium.

All the metallic chlorides, excepting those of the metals of the alkalis and of the earths, are reduced when sufficiently heated in a brisk current of hydrogen. In many cases the reduction is easily effected, and this process is occasionally resorted to as a means of procuring certain metals in a state of purity. Iron, for example, may be obtained in fine cubic crystals by reducing the protochloride of the metal in this manner. It is necessary, however, to maintain a current of hydrogen of sufficient rapidity to carry away the hydrochloric acid from the reduced metal, as otherwise, in most cases, the chloride would be reproduced by the decomposition of the acid. Other particulars relating to the chlorides have been already mentioned (313, 316).

(445) *Estimation of Chlorine in Metallic Chlorides.*—Chlorine is almost always estimated in the form of chloride of silver, 100 parts of which represent 24.74 of chlorine. The solution should be acidulated with nitric acid, and gently warmed, and then the nitrate of silver should be added. If iodine or bromine be present, it will be precipitated with the chlorine and must be determined separately, and the corresponding weight of iodide or bromide of silver deducted.

The composition of an insoluble chloride or of a basic chloride may be determined by boiling a given weight of the compound with pure solution of potash, and determining the quantity of chlorine in the alkaline solution by means of nitrate of silver: before adding the solution of silver, the alkaline liquid must be filtered from the undissolved metallic oxide, and acidulated with nitric acid.



(446) The BROMIDES (328, 329) closely resemble the chlorides in chemical characters: the bromides of the alkalis and alkaline earths may be prepared by digesting them with bromine in slight excess; a bromide and a bromate of the metal are formed, and by gentle ignition the bromate is decomposed, leaving a pure bromide: a small quantity of charcoal may be added previous to the ignition, by which the decomposition of the bromate is more easily effected. The bromide is removed from the excess of charcoal by solution in water. The other bromides may be procured by acting upon the metals by bromine, either in a dry state, or in the presence of water. They are also easily formed by dissolving the oxides or the carbonates in hydrobromic acid.

Bromine may be precipitated from its solutions, and, in the absence of chlorine, its quantity may be estimated by means of nitrate of silver, which occasions a white precipitate of bromide of silver, 100 parts of which contain 41.47 of bromine. If chlorine be present, the precipitate will consist of a mixture of the bromide and chloride of silver, it must be collected and weighed, then digested with metallic zinc, and a drop or two of sulphuric acid; in a day or two the zinc will have reduced the bromide and chloride to metallic silver: this must be well washed, dried, and weighed. It should be wholly soluble in nitric acid, as if it be not, part of the precipitate has escaped decomposition.

From the above data the relative proportions of the bromide and of the chloride of silver may be calculated: let  $m$  be the weight of the mixed bromide and chloride, and let  $s$  be the weight of the reduced silver; then if  $x$  represent the proportion of bromide and  $y$  that of chloride of silver,

$$m = x + y, \text{ and } s = \frac{108}{143.5} x + \frac{108}{184} y,$$

consequently  $x$ , or the bromide of silver in the mixture,  $= m - y$ , and  $y$ , or the chloride of silver in the mixture,  $= 5.1634 s - 3.2247 m$ .

(446 *bis*) The IODIDES may be formed by processes analogous to those employed for the bromides: the insoluble iodides, such as those of silver and lead, may be obtained from solutions of the iodide of potassium, by admixture with a solution of the metallic salt.

The iodides exhibit a strong tendency to form double salts, the iodides of the alkaline and electro-positive metals combining readily to form crystallizable double iodides with those of the electro-negative metals, such as those of silver, mercury, and lead. The

iodides also form double compounds with the oxides and chlorides; for example, there are several compounds of the iodide with the oxide of lead; and a combination of bichloride of tin with the protiodide of that metal may be obtained in orange-coloured crystals; ( $\text{SnI}$ ,  $\text{SnCl}_2$ ).

The quantity of iodine in a solution which contains iodides, if chlorides be absent, may be estimated by the addition of nitrate of silver slightly acidulated with nitric acid: the resulting buff-coloured iodide of silver, when collected and dried, contains 54.0 per cent. of iodine. If chlorine or bromine be present, the iodine must be precipitated by means of nitrate of palladium; the precipitate must be allowed to subside during ten or twelve hours, and it may then be collected on a filter. It contains 70.0 per cent. of iodine.

(447) FLUORIDES.—The general properties of these compounds have been already stated (338). The fluorides are usually prepared by the direct combination of hydrofluoric acid with the metallic oxide. Those which are insoluble may be procured by mixing a solution of the metallic salt with one of fluoride of potassium or of sodium.

*Estimation of Fluorine.*—A simple method of detecting and of approximatively estimating fluorine, when present even in very small quantities, has been proposed by Dr. G. Wilson. The following is the process, slightly modified:—the substance, if it does not already contain silica, is mixed with pounded glass, placed in a retort, and made into a thin cream with oil of vitriol; the mixture is next heated, and distilled into a flask containing a solution of ammonia; the fluoride of silicon comes over, and is immediately decomposed: on evaporating the liquid in the flask to dryness on a water bath, the silica is rendered insoluble, and can be collected and weighed, whilst the fluoride of ammonium may be dissolved out with a little water, and the presence of fluorine shown by mixing it with oil of vitriol; the vapour which is evolved produces the usual corrosive action of hydrofluoric acid on glass (338): the proportion of silica in the insoluble residuc to the fluorine, however, is not very uniform.

(448) NITRIDES.—It is not improbable that the fulminating compounds, obtained by digesting the hydrated oxides of gold, of silver, and of platinum, in solution of ammonia, may owe their explosive character to the formation of a nitride: the composition of these bodies has been but imperfectly investigated, on account of their explosive character. So weak is the affinity of nitrogen for metallic bodies, that a very slight alteration of circumstances suffices

to restore it suddenly to the gaseous state. Nitride of copper is formed by passing dry ammonia over oxide of copper, at a temperature not exceeding  $480^{\circ}$ , in which case water is formed at the expense of the hydrogen of the ammonia and the oxygen of the oxide, and part of the nitrogen escapes; thus,  $6 \text{ CuO} + 2 \text{ NH}_3 = \text{Cu}_3\text{N} + 6 \text{ HO} + \text{N}$ . Nitride of mercury may be prepared by passing ammonia over oxide of mercury in a similar manner.

(449) The PHOSPHIDES of the metals are of comparatively small importance: they are never met with in the native state. The phosphides of the metals of the alkalis and of the alkaline earths, decompose water when thrown into it; self-lighting phosphuretted hydrogen is disengaged, and a hypophosphite of the base is retained in solution. They may generally be formed by reducing the phosphates by heating them with carbon. In some cases, as for example in that of phosphide of calcium, the phosphide is formed by heating the oxide strongly, and driving the vapour of phosphorus over it; in this case it is mixed with a large proportion of phosphate of lime. The insoluble phosphides may often be obtained by transmitting a current of phosphuretted hydrogen through a solution of the salt of the metal in water: phosphides of copper and silver may be thus obtained.

When heated in air the phosphides are converted into phosphates, or into phosphoric acid, while the metal is liberated.

“(450) CARBIDES.—The only carbides of importance are those of iron, which will be considered in detail when treating of that metal. Manganese, palladium, iridium, and a few other metals also combine with carbon; generally speaking, these carbides are more fusible than the metals which enter into their formation.

SILICON AND BORON form with the metals analogous compounds of small importance.

(451) HYDRIDES.—Hydrogen is not known to combine with more than three metals: viz., arsenic, tellurium, and antimony. These compounds are gaseous, and all are decomposed by a red heat into metal and hydrogen gas. A solid hydride of arsenic is also said to exist. A few metals, such as zinc and potassium, appear under peculiar circumstances to undergo partial volatilization along with the hydrogen at the moment that this gas is liberated.

### § III. THEORY OF SALTS.

(452) It has already been stated (6) that any substance which is produced by the union of a base with an acid is termed a salt.

It is, however, necessary to examine more minutely into the nature both of bases and of acids, and the compounds formed by their combination with each other.

By the word *base*, is meant a body always of a compound nature, very frequently an oxide of a metal, which is capable of uniting with an acid, and of more or less completely neutralizing the distinctive characters of that acid. A base, however, is not necessarily a metallic oxide; ammonia, quinine, and morphia, for example, are powerful bases, but they contain no metallic substance.

Besides the class of salts formed by the combination of an acid with a base, there is a numerous and important series in which neither acid nor base is present, and of which common salt is a familiar instance. We proceed to indicate the points of difference and agreement between these two kinds of salts.

(453) *Oxyacids and Hydracids*.—When Lavoisier imposed the name of oxygen upon one of the constituents of the atmosphere, he supposed that the presence of that energetic body was essential to the existence of an acid, and this view was supported by the known composition of the principal acids, such as the sulphuric, the sulphurous, the nitric, the carbonic, the phosphoric, and the boracic acids. An acid was then considered to be an oxidized body more or less soluble in water, with a sour taste, capable of reddening vegetable blues, and entering into combination with the alkalies, the distinctive properties of which it neutralized.

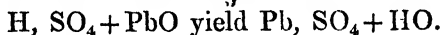
By degrees, however, acids were discovered, in which no oxygen could be detected; such, for example, as the hydrochloric, the hydriodic, and the hydrobromic, into the composition of which hydrogen enters; yet these bodies were found <sup>in other</sup> to correspond perfectly with the above definition, and possess all the characters of powerful acids. To meet this objection, the theory was modified, and the acids were divided into two great classes, the first of which comprised the *oxyacids*, such as the sulphuric, nitric, and others of analogous composition, in which it was supposed that the acid properties depended on the presence of oxygen; the second class included the *hydracids*, such as the hydrochloric and hydriodic acids, in which the acidifying principle was assumed to be hydrogen. It was noticed, that when bodies belonging to either of these classes combine with metallic compounds, and form neutral combinations, the acids do not unite directly with the metals; the combination is always with their *oxides*: sulphuric acid, for example, has no action upon metallic copper, but it quickly dissolves its oxide, forming the

blue solution of sulphate of copper. On applying heat so as to render the salt anhydrous, it was found that the salts of the oxyacids (of which sulphate of potash may be taken as the type) might be represented under the form  $\text{KO}, \text{SO}_3$ , which supposes the union of 1 equivalent of the dry acid with 1 equivalent of the alkaline base; while a hydracid (such for instance as hydrochloric acid) if united with a base, such as soda, yields a body like common salt, which when dry contains neither hydrochloric acid nor soda, the radicle of the acid being left in combination with the metal itself;  $\text{NaO} + \text{HCl} = \text{NaCl} + \text{HO}$ . Thus, in the case of the salts of the hydracids, it will be observed, that the oxygen of the oxide is precisely sufficient to convert the hydrogen of the acid into water: this union, indeed, actually takes place, and the water which they form is expelled on the application of heat. It thus appears that although compounds formed by the union of an acid with a base may be correctly designated salts, it would lead to a strange anomaly were a salt to be defined as a compound of any acid with a base, since such a definition would exclude common table-salt—the very substance from which the term salt was originally derived: table-salt, it is true, may be formed by the union of hydrochloric acid with the base, soda, but the compound when dry contains neither the acid nor the alkali which was used.

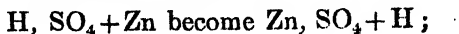
To obviate this difficulty, it was proposed to subdivide salts into two classes, the first being formed by the union of an oxide with an oxyacid, like sulphate of potash; these were termed *oxysalts*; the other class being produced by the combination of a metal with the characteristic element in a hydrogen acid. The salts of the second class being composed upon the same plan or type as sea-salt, were termed *haloid* salts (from  $\alpha\lambda\varsigma$ , the sea), and the elements chlorine, bromine, iodine, and fluorine, which were capable of producing such compounds, were termed *halogens*. This distinction is generally recognised by chemical writers of the present day.

(454) *Binary Theory of Salts*.—The foregoing observations seem to prove that there is a marked difference between the composition of the oxyacid and the hydracid series of salts. The separation of salts into two classes, one consisting of the salts of the oxyacids, and the other of those of the hydracids, is not, however, indispensable. A hypothesis was advanced by Sir H. Davy, which reduces all salts under one class, and refers them all to the hydracid type. Upon this view—frequently termed *the binary theory of salts*—all the acids, or at least all the hydrated acids, are regarded as salts containing

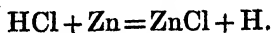
hydrogen in the place of a metal, so that oxide of hydrogen, or water, acts the part of a feeble base to the dry acids. It is remarkable that such of the oxyacids as can be obtained in the dry or anhydrous form, such for example as the sulphuric, the nitric, the phosphoric, the carbonic, and the boracic acids, do not possess the properties generally admitted to constitute the true acid character. Dry sulphuric acid, for instance, does not redden dry litmus; it may be moulded in the fingers without injury; but when once it passes into the hydrated form, which it speedily does by absorbing moisture from the air, it corrodes all organized substances with great activity. Dry carbonic acid is also without action on litmus. When such acids are combined with water, by a slight modification of the formula they may be represented as hydracids; *e.g.*, oil of vitriol ( $\text{H}_2\text{O}, \text{SO}_3$ ), may be expressed as  $(\text{H}, \text{SO}_4)$ , corresponding with hydrochloric acid  $(\text{H}, \text{Cl})$ : their hydrates, when heated in contact with a base or a metallic oxide, give off one equivalent of water, in a manner precisely analogous to the hydracids already examined. One equivalent of oil of vitriol treated with 1 equivalent of oxide of lead would thus produce an equivalent of sulphate of lead and an equivalent of water, as thus appears—



Upon this theory, the compounds which chemists have been in the habit of considering as hydrated acids, would be regarded as salts composed of a compound radicle (consisting of the anhydrous acid + an equivalent of oxygen) united with an equivalent of hydrogen. The other salts of the acid are formed from these hydrogen compounds by the displacement of the hydrogen by the different metals which enter into the composition of the various salts, and which are indicated by their respective names. A very simple explanation is in this manner afforded of the liberation of hydrogen when diluted sulphuric acid is acted upon by zinc; the zinc simply enters into combination with the radicle of the acid, and displaces the hydrogen. Thus—



and the reaction is, upon this view, perfectly analogous to that of the same metal upon hydrochloric acid;—



This simple and elegant hypothesis long remained an unsupported and fruitless speculation; but within the last few years the

researches made in the department of organic chemistry have greatly strengthened its probability ; and it has also received powerful experimental confirmation from the voltaic researches of Prof. Daniell. It was found by Mr. Daniell and myself that if a current of voltaic electricity from two or three cells were transmitted through fused nitrate of silver, the salt was readily decomposed, but that metallic silver in crystals was deposited upon the platinode, whilst the oxygen and the nitric acid passed to the zincode, so that under these circumstances, the nitrate of silver ( $\text{AgO}, \text{NO}_3$ ) was resolved into ( $\text{Ag}, \text{NO}_3$ ), the  $\text{NO}_3$  breaking up at the moment of its liberation into red fumes of peroxide of nitrogen and free oxygen gas. Other experiments which further illustrate this point, will be described hereafter.

A good instance of the advantageous application of Davy's theory is afforded by the different modifications of phosphoric acid, the leading peculiarities of which have been already described (369). The three varieties of phosphoric acid have been distinguished as 1, the monobasic or metaphosphoric acid, which combines with 1 equivalent of a metal; the soda-salt may be represented as ( $\text{Na}, \text{PO}_3$ ); 2, the dibasic or pyrophosphoric acid, the radicle of which unites with 2 equivalents of metal, the soda salt of which may be regarded as ( $2 \text{ Na}, \text{PO}_4$ ); and 3, the tribasic, or common phosphoric acid, the radicle of which requires 3 equivalents for saturation, and the soda salt in this case would have the formula ( $3 \text{ Na}, \text{PO}_4$ ). Each modification forms a corresponding phosphate with hydrogen, the three compounds with hydrogen being usually considered as three distinct hydrates of phosphoric acid, or phosphates of water :  $\text{HO}, \text{PO}_3$  being the monophosphate or metaphosphate of water,  $2 \text{ HO}, \text{PO}_4$  being the diphosphate or pyrophosphate of water, and  $3 \text{ HO}, \text{PO}_4$  being the triphosphate, or ordinary phosphate of water. These three different proportions of water admit of being displaced by a corresponding number of equivalents of other bases. Much difficulty in comprehending this anomalous relation of phosphoric acid to water is however removed if each modification be considered to possess a different radicle, which regulates the varying constitution of the three classes of salts ; a view which voltaic researches have strengthened by direct experiment (Daniell and Miller, *Phil. Trans.* 1844, p. 1). Upon this theory it is evident that so long as each radicle possesses its peculiar constitution it will require its own characteristic number of equivalents of base to form a salt : on the old hypothesis, however, there appears to be no satisfactory reason why in the aqueous solutions of the acid sometimes one equivalent,

sometimes two, and sometimes three equivalents of water should be displaced by a base. In order to render this evident, it must be remembered that water, when in combination, plays several distinct parts (291). The water, chemically united with these hydrates of phosphoric acid, acts the part of a base, and is in a condition very different from the water which many crystallized salts contain in the dry or solid form, and which is essential to the possession of their peculiar crystalline shape. Water under this modification is called *water of crystallization*.

Ordinary rhombic phosphate of soda presents water acting both as a base and as water of crystallization. The constitution of this salt may be represented by the formula ( $\text{Na}_2\text{H}, \text{PO}_8, 24 \text{ H}_2\text{O}$ ). The 24 equivalents of water of crystallization are expelled below  $300^\circ \text{F}$ . If the residue be dissolved in water, the solution presents all the characters of a solution of the original salt, and by evaporation the phosphate of soda is recovered in its original crystalline form. If, however, the dry residue,  $\text{Na}_2\text{H}, \text{PO}_8$ , be heated to redness, an additional equivalent of water escapes; the radicle,  $\text{PO}_8$ , is partially deoxidized by the hydrogen; a new radicle,  $\text{PO}_7$ , is formed, and enters into combination with  $\text{Na}_2$ , and on dissolving it in water, a new salt, the pyrophosphate of soda, is produced;  $\text{Na}_2\text{H}, \text{PO}_8$  become  $\text{Na}_2, \text{PO}_7 + \text{H}_2\text{O}$ . In like manner if the acid phosphate of soda,  $\text{NaH}_2, \text{PO}_8$ , be heated to redness, the two equivalents of hydrogen remove two equivalents of oxygen from the radicle,  $\text{PO}_8$ , which then becomes  $\text{PO}_6$ ;  $\text{NaH}_2, \text{PO}_8 = \text{Na}, \text{PO}_6 + 2 \text{ H}_2\text{O}$ .

(455) *Objections to the Binary Theory*.—Notwithstanding the ingenuity of the foregoing theory, and the advantages which it offers in the explanation of certain modes of decomposition, it is open to many serious objections; and indeed it cannot be regarded as a correct representation of the composition of a salt under all circumstances.

A few of these objections may be pointed out:—

1. None of the compound radicles,  $\text{SO}_4$ ,  $\text{NO}_6$ ,  $\text{CO}_3$ , have been obtained in an isolated form, nor is it probable that they ever will be.

2. It appears to be highly improbable that a body of such powerful affinities as potash should, in carbonate of potash for example, part with its oxygen to a substance which, like carbonic acid, exhibits no tendency to further oxidation, so that  $\text{KO}, \text{CO}_2$  should become  $\text{K}, \text{CO}_3$ .

3. Further, if this theory be applied to the ordinary salts of the



oxyacids, no reason can be assigned why it should not be equally applicable to the corresponding sulphur compounds, and then the contradictions and inconsistencies arising from its application become still more apparent.

The conclusion which a careful review of the arguments adduced seems to render most probable is this: viz., that a salt, when once formed, must be regarded as a whole; it can no longer be looked upon as consisting of two distinct parts, but as a new substance, maintained in its existing condition by the mutual actions of all the elements which compose it. These different elements are not all united among each other in every direction with an equal amount of force. As in a crystal there are certain directions in which the mass admits of cleavage with greater facility than in others, and as two or three different directions of cleavage may be found in the same crystal by varying the direction in which the force is applied, so in the same salt there are directions in which it yields to the application of chemical force more readily than others, and according as that chemical force is applied in one way or in another, the compound splits up into simpler substances, the nature of which will vary according to the mode which has been selected for effecting its decomposition.

For example, if a strong acid, such as nitric acid, be poured upon carbonate of potash, carbonic acid is liberated abundantly, and nitrate of potash is produced;  $\text{KO}, \text{CO}_2 + \text{NO}_5 = \text{KO}, \text{NO}_5 + \text{CO}_2$ ; but if another portion of the same carbonate of potash be mixed with charcoal, and heated in an iron retort to whiteness, metallic potassium and carbonic oxide are the results;  $\text{KO}, \text{CO}_2 + 2 \text{C} = \text{K} + 3 \text{CO}$ . Again, if a solution of carbonate of potash be subjected to electrolysis by the aid of the voltaic battery, the salt splits up into potassium (which is immediately oxidized by the water in the midst of which it is liberated), and into  $\text{CO}_3$ , which is as instantly resolved into oxygen gas and carbonic acid;  $\text{KO}, \text{CO}_2$  becoming  $\text{K}, \text{CO}_3$ , and  $\text{K} + \text{HO}$  giving  $\text{KO} + \text{H}$ , whilst  $\text{CO}_3$  becomes  $\text{CO}_2 + \text{O}$ . The probability therefore is, that neither the old nor the new view is absolutely correct, but that each may in turn well represent the salt when subjected to the influence of particular circumstances. It may therefore readily be conceded that the binary theory may in certain cases elucidate the decompositions observed, notwithstanding the difficulties which prevent its adoption as a correct representation of the molecular arrangement of saline compounds in general.

Binary compounds are such as consist of two elements only; chloride of sodium, ( $\text{NaCl}$ ), therefore, is a binary compound; and if all salts be assimilated to this type, it is assumed that the grouping of their molecules resembles that which occurs in this binary compound. Upon this view all salts consist of two portions: one comprising the distinctive constituents of the acid, and consisting either of a non-metallic elementary substance, chlorine,  $\text{Cl}$ , for example, or else an equivalent compound body (suppose it be sulphur,  $\text{SO}_4$ ), which is termed the *radicle* of the salt; the other is either a metal (sodium,  $\text{Na}$ , for instance), or else a compound like ammonium, ( $\text{NH}_4$ ), equivalent to a metal, and which Mr. Graham has proposed to call the *basyle* of the salt. The hydrated acids are regarded merely as salts of hydrogen, which in combination comport itself like a metal, and which, for aught that is known to the contrary, may really be a metallic vapour.

(456) *Sulpho-Salts*.—The preceding remarks have been made with almost exclusive reference to those salts into the composition of which oxygen enters. There is however a numerous series of compounds parallel to these oxy-compounds, but in which sulphur enters into combination with the metal; and for each equivalent of oxygen in the series of the oxy-salts 1 equivalent of sulphur is substituted in the corresponding compound in the sulphur series. Generally speaking the sulphur-salts are of subordinate importance to the oxy-compounds; they are often decomposed by water, and have been the subject of much less study and research. Many chemists regard these compounds as salts in which the electro-positive sulphides, such as the protosulphide of potassium, &c., act the part of bases; and the electro-negative sulphides, such as the higher sulphides of arsenic and antimony, act as acids.

(457) *Varieties of Salts*.—Salts are usually spoken of as *neutral*, *acid*, or *basic*; but though these terms are in general use, there is some ambiguity in the manner in which they are applied.

(458) *Neutral Salts*.—The idea of neutrality implies that the peculiar characters of the acid and of the alkali have each disappeared as a result of combination, and one of the usual means by which this neutralization in properties is judged of consists in observing the effect which is produced upon certain vegetable colours when mixed with a solution of the salt.

The blue colour of litmus, for example, is changed to red by the action of an acid, whilst the colour of litmus reddened by an

acid becomes blue if it be mixed with an alkali. The yellow colour of turmeric is changed to brown when mixed with an alkali, but the yellow is restored if the alkali be caused to combine with an acid. A salt which affects neither the blue of litmus nor the yellow of turmeric is said to have a neutral reaction. But chemists are in the habit of regarding many salts as neutral in composition which are not neutral in their action upon coloured tests. The basic properties of different metallic oxides vary considerably in intensity. Equal quantities of the same acid, according as it is neutralized by equivalent quantities of a weak base or of a strong one, will differ considerably in their action upon coloured tests; for example, 54 parts of nitric acid in combination with 47 parts of potash furnish nitrate of potash, which, when dissolved in water, does not affect the colour either of blue or of reddened litmus paper. It is, therefore, neutral in its reactions upon coloured tests. In the case of nitrate of potash, the proportion of oxygen in the potash to that in the nitric acid is as 8 parts to 40, or as 1 equivalent is to 5.

Salts of nitric acid in which the oxygen of the base bears this proportion to that in the acid, are regarded as neutral in composition, whatever may be their action on vegetable colours. Now if the same proportion of nitric acid be caused to combine with an equivalent of oxide of lead, 112 parts of oxide of lead will combine with the 54 of nitric acid, and will form a salt in which, as in nitrate of potash, 1 equivalent of oxygen is present in the base for every 5 equivalents of oxygen in the acid. This salt, therefore, is neutral in composition, though if dissolved in water it reddens litmus, and has an acid reaction.

The change in the tint of the coloured test is therefore not to be regarded as an absolute proof of neutrality or acidity in a salt. The change of colour which the litmus experiences, even from a salt of neutral composition, is readily explained. Blue litmus is itself a species of salt, resulting from the combination of an alkaline or earthy base with a feeble vegetable acid which is, naturally of a red colour, but which becomes blue when it is neutralized by an alkali. When a powerful acid, such as the nitric or sulphuric, is mixed with this blue colouring matter, the strong acid seizes upon the base which the litmus contains, and displaces the litmus acid which appears of its natural red hue; but on the addition of an alkali, the blue is restored by the combination of the newly added base with the litmus acid. Again, if a salt with a strong acid and a comparatively feeble base be mixed with the blue litmus, the strong acid of the salt seizes upon part of the base which is in combination

with the litmus, and liberates the litmus acid, which appears of a more or less intense red, according as the base of the neutral salt has given up more or less of its acid.

For analogous reasons it sometimes happens that a salt which is neutral in composition may exhibit characters in which the base preponderates to a greater or less extent. Carbonate of potash, ( $\text{KO}, \text{CO}_2$ ), is neutral in composition, but it appears to be basic in its action upon the yellow colour of turmeric paper, which it renders powerfully brown, and it immediately restores the blue tinge to reddened litmus.

The three salts which have just been cited to illustrate these points are all of them instances of the most usual form of salt, in which 1 equivalent of a protoxide is united with 1 equivalent of an acid to form the neutral salt. But salts exist in which the base consists of a sesquioxide, and in such cases 3 equivalents of the acid are needed to 1 of the base in order to produce a salt which is neutral in composition.

The sulphates will afford a good illustration of these modes of combination. A neutral sulphate of a protoxide, such as sulphate of potash ( $\text{KO}, \text{SO}_3$ ), requires 1 equivalent of oxygen in the base to 3 equivalents of oxygen in the acid; and contains 1 equivalent of acid to each equivalent of the base.

But in the case of a sesquioxide, such as alumina,  $\text{Al}_2\text{O}_3$ , 3 equivalents of acid are combined with each equivalent of alumina in order to form the neutral sulphate of this base,  $\text{Al}_2\text{O}_3, 3 \text{SO}_3$ ; and the neutral sulphate of peroxide of iron ( $\text{Fe}_2\text{O}_3, 3 \text{SO}_3$ ) has a similar composition: in salts of this kind, however, the rule is still observed, that the number of equivalents of oxygen in the base is to that of those in the acid as 1 to 3. The sulphate of alumina and the persulphate of iron not only redden litmus paper powerfully, but they have an acid as well as an astringent taste.\*

(459) *Acid Salts*.—If a quantity of oxalic acid be divided into two equal portions, one of which is dissolved in water, and mixed

\* The tendency of the sesquioxides to require so large a proportion of acid has been supposed to afford another argument in favour of the binary theory of salts. It will be seen that the composition of the neutral persulphates readily admits of being represented upon the binary view in harmony with the sulphates of the protoxides. Sulphate of peroxide of iron, for example, ( $\text{Fe}_2\text{O}_3, 3 \text{SO}_3$ ) might be written ( $\text{Fe}_3, 3 \text{SO}_3$ ). This argument, however, is entitled to but little weight, as many salts of the sesquioxides are known in which the proportion of the acid is less than in these instances; and, indeed, both alumina and peroxide of iron form, with sulphuric acid, soluble compounds, which contain but 1 equivalent each of acid and of base.

with a solution of potash until the liquid becomes neutral in its reaction upon litmus, a salt is formed which, on evaporation, may be obtained crystallized in six-sided prisms, which consists of the neutral oxalate of potash ( $K_2O, C_2O_3 + HO$ ). If this salt be redissolved in water, and the second portion of oxalic acid be added to it, chemical union will occur; the resulting liquid will be found to have a sour taste, to redden litmus powerfully, and on evaporation to yield a new salt, which crystallizes in rhomboidal prisms, containing exactly twice as much acid as the first salt; this is the binoxalate, or acid oxalate, of potash ( $K_2O, HO, 2 (C_2O_3) + 2 HO$ ).

Again, if the neutral sulphate of potash ( $K_2O, SO_3$ ) be dissolved in hot sulphuric acid, tabular plates of a new, fusible, and strongly acid salt will crystallize out as the liquid cools, and the bisulphate of potash will be formed ( $K_2O, HO, 2 SO_3$ ). This salt contains, for each equivalent of oxygen in the potash, 6 equivalents of oxygen in the acid, or double the amount which is present in the neutral sulphate. If an attempt be made to form a similar salt by dissolving nitrate of potash in nitric acid, the experiment will fail, for the nitre will be found to crystallize out unchanged.

It is thus apparent that in certain cases the acid combines with the base in two proportions, in others it refuses to do so in more than one.

It usually happens that acid salts contain, in addition to the acid and base, a certain quantity of water, as occurs for instance in the bisulphate and the binoxalate of potash. This water is by no means an unimportant constituent, as it takes the place of the metallic oxide on these occasions: and it is because the basic properties of water are so feeble, that the acid character predominates to so great a degree in such salts.

(460) *Polybasic Acids*.—The formation of some kinds of acid salts may be elucidated by the following considerations. Most of the inorganic acids combine with bases in such a manner that 1 equivalent of the acid is united with 1 equivalent of metallic oxide, so that they may be termed *monobasic acids*. Of this class of acids the nitric is a good example.

Certain acids, however, of which an instance has already presented itself in the pyrophosphoric, possess the power of combining with 2 equivalents of base, and are hence termed  *dibasic*. Numerous acids of this class are found among those obtained from the vegetable and the animal kingdoms; tartaric acid and malic acid are examples of this kind.

The common phosphoric acid contained in the crystallized

phosphate of ~~the~~ of commerce, is the representative of a third class of acids, which combine with 3 equivalents of base, and are hence termed *tribasic*.

There are many organic acids which belong to this class; the citric furnishes a good instance. It is not necessary that the two or the three equivalents of base which the salts of the dibasic or tribasic acids contain should consist of the same metallic oxide. Indeed, it has already been shown, in the case of the various phosphates, that several bases may coexist in the same salt, in definite proportions. There is, for example, a pyrophosphate of soda and water, composed of  $\text{NaO}$ ,  $\text{HO}$ ,  $\text{PO}_5$ , in which 1 equivalent of hydrogen supplies the part of 1 equivalent of sodium; and in the microcosmic salt ( $\text{NaO}$ ,  $\text{NH}_4\text{O}$ ,  $\text{HO}$ ,  $\text{PO}_5 + 8 \text{HO}$ ) we have a tribasic phosphate of soda, oxide of ammonium, and water, where each of the 3 equivalents of base differs from the others. It is worthy of remark that, in the salt last named, two of these bases, viz., soda and oxide of ammonium, are isomorphous.

Now it frequently happens, as in microcosmic salt, that water is one of the bases present in the salt and, when such is the case, the salt, when dissolved in water, often has a sour taste, and strongly reddens litmus paper. One of the most common varieties of what are termed acid salts is thus formed. Cream of tartar, or, as it is often called, bitartrate of potash, offers a good illustration of this kind of salt.

Cream of tartar is a sparingly soluble crystallizable compound, of an agreeable acidulous taste, which consists of  $\text{HO}$ ,  $\text{KO}$ ,  $\text{C}_8\text{H}_4\text{O}_{10}$ , being, in fact, a dibasic tartrate of potash and water; if now it be dissolved in hot water, and another equivalent of potash be added, the water is displaced by the second equivalent of potash, all the acid taste disappears, and neutral tartrate of potash ( $2 \text{KO}$ ,  $\text{C}_8\text{H}_4\text{O}_{10}$ ), a salt, no longer affecting the colour either of litmus or of turmeric paper, is produced. An equivalent quantity of carbonate of potash may be substituted for caustic potash with equal effect, as it will be decomposed, and the carbonic acid will be expelled with effervescence. Carbonate of soda may be substituted for the carbonate of potash, but in this case a different salt, known as Rochelle salt, the tartrate of soda and potash, will be formed, ( $\text{KO}$ ,  $\text{NaO}$ ,  $\text{C}_8\text{H}_4\text{O}_{10} + 10 \text{aq}$ ).

Acid salts, however, though generally formed, like cream of tartar, from a dibasic acid with which 1 equivalent only of a powerful base has combined, the place of the second equivalent being supplied by an equivalent of water, are not always so pro-

duced. A bisulphate of potash, which is anhydrous, may be obtained ( $\text{KO}, 2 \text{SO}_3$ ); and bichromate of potash always occurs in the anhydrous form. Mr. Graham has endeavoured to account for the formation of some other acid salts in a different manner, which will be noticed presently.

(461) *Double Salts*.—The description of these polybasic acids has presented us with certain cases in which *double salts* are formed. There are several varieties of double salts. The most common are those which are produced by the union of two dissimilar bases with the same acid. These varieties, however, are confined within certain limits. It is not possible to form double salts *ad libitum*, by bringing 2 equivalents of any acid in contact with 1 equivalent each of any two bases. Chemists assume that when two isomorphous bases, such as soda and potash, combine with the same acid in the proportion of 1 equivalent of each base to form a double salt (like Rochelle salt), the acid in question is dibasic. The larger number of double salts which have been produced are thus formed by the combination of different bases with polybasic acids.

The formation of another remarkable series of double salts, particularly investigated by Graham, appears to be directly connected with the mode in which water attaches itself to certain salts. In most cases the water of crystallization may be expelled from a salt by exposing it to a temperature not exceeding  $212^\circ$ . This, however, does not always happen: sometimes all the water of crystallization may thus be expelled with the exception of a single equivalent, which requires a much higher heat for its expulsion, although in these cases it does not appear to act in any degree as a base. Under these circumstances it was found that this last equivalent of water might readily be displaced by adding to the salt an equivalent of certain anhydrous salts. An excellent illustration of such a method of the formation of double salts is afforded in the case of a certain class of the sulphates. All the sulphates of bases isomorphous with magnesia are capable of forming double salts of this nature with some anhydrous sulphate not isomorphous with this class, such, for instance, as the sulphate of potash.

When sulphate of magnesia ( $\text{MgO}, \text{SO}_3, \text{HO}, 6 \text{aq}$ ) is heated to  $212^\circ$ , six out of its seven equivalents of water are expelled, but the seventh equivalent is retained until the temperature is raised considerably. If, however, an equivalent of sulphate of magnesia and an equivalent of sulphate of potash be separately dissolved in water, mixed while hot, and allowed to crystallize, a new

double salt ( $\text{MgO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6 \text{ aq}$ ) is deposited, having the same crystalline form as sulphate of magnesia, but it contains only 6 equivalents of water of crystallization. The seventh equivalent has been displaced by the sulphate of potash, and has hence been termed, by Graham, constitutional, or *saline water*.

A similar substitution takes place with sulphuric acid itself, or sulphate of water; when diluted till of the specific gravity of 1.78, it consists of  $\text{HO}, \text{SO}_3 + \text{HO}$ ; and from the circumstance of its readily forming well-defined crystals when cooled to a temperature of  $40^\circ \text{ F.}$ , it is often termed *glacial sulphuric acid*: this compound consists of 1 equivalent of sulphate of water with 1 equivalent of saline water. If a solution of sulphate of potash be added to this glacial acid, the liquid, when evaporated, yields the well known salt, bisulphate of potash. This compound, consisting of sulphate of water and sulphate of potash, may be regarded as a double salt, in which the sulphate of potash has displaced the saline water from the glacial acid;  $\text{KO}, \text{SO}_3 + \text{HO}, \text{SO}_3, \text{HO} = \text{HO} + (\text{HO}, \text{SO}_3 + \text{KO}, \text{SO}_3)$ : the water in the bisulphate is in the form of basic water. It is by the union of the hydrated acid with a metallic salt that acid salts in general are formed. The bicarbonates, binoxalates, and many other similar compounds, prove on examination, not to be mere salts with excess of acid, but true double salts of this class, analogous to neutral salts in composition. Bicarbonate of potash, for instance, may be represented as thus constituted:  $\text{KO}, \text{CO}_2 + \text{HO}, \text{CO}_2$ ; and binoxalate of potash,  $\text{KO}, \text{C}_2\text{O}_3 + \text{HO}, \text{C}_2\text{O}_3 + 2 \text{ aq}$ . As already mentioned, double salts of this kind are never formed by two isomorphous bases.

There is another well-known variety of double salts, in which it is not necessary that the component salts should contain similar oxides, or even a similar number of equivalents of the radicle of the acid. In this way sulphates of sesquioxides often unite with the sulphates of protoxides to form well-characterized double salts; a striking example of this kind is afforded in the important tribe of alums. Common alum consists of 1 equivalent of sulphate of potash and 1 equivalent of sesquisulphate of alumina with water of crystallization ( $\text{KO}, \text{SO}_3 + \text{Al}_2\text{O}_3, 3 \text{ SO}_3 + 24 \text{ aq}$ ); and numerous other salts, having the same crystalline form, and of similar composition, might be mentioned.

There are a few instances of two different acids being united to one base, but they are neither sufficiently numerous nor important to merit lengthened notice, and are more frequently met with among natural, than artificial combinations.



Instances are common in which two different haloid salts unite with each other; compounds of this description are most usual between the chlorides, iodides, and bromides of the less oxidizable metals with those of the metals contained in the alkalies and earths: the double chloride of platinum and potassium ( $\text{KCl}$ ,  $\text{PtCl}_2$ ), and the double iodide of mercury and potassium ( $\text{KI}$ ,  $\text{HgI}$ ), are good instances of such compounds. Bonsdorff proposed to consider these compounds in the light of salts in which the chloride or iodide of the electro-negative metal (platinum, gold, &c.) acted the part of an acid towards the electro-positive chloride (chloride of potassium, sodium, &c.); but this view is not tenable. Such salts are never resolved by electric action into their constituent chlorides, and the acid reaction of the higher chlorides is not neutralized or modified by combination with the chlorides of the alkaline metals; in fact, the constituent chlorides themselves are salts.

Many double salts may be formed by fusion with each other, although if the attempt be made to crystallize them from a solution containing equivalent quantities of the two salts, the attempt is unsuccessful. Chloride of sodium, for example, may be melted with an equivalent amount of chloride of calcium, of strontium, or of barium; and in either case a compound salt is obtained, which has a much lower fusing point than either of the chlorides separately, but the double salt is decomposed when it is dissolved in water.

(462) *Subsalts*.—A very different series of saline compounds still remains for consideration, and in these the proportion of base predominates over that of the acid; they are usually designated subsalts. The theory of the formation of these compounds is very imperfect. In certain cases the formation of a subsalt admits of the explanation offered by Mr. Graham. He assumes that a portion of the water of crystallization of the neutral salt has been displaced by a basic metallic oxide. It is a well known fact that in analogous compounds, isomorphous bodies are frequently found displacing each other in composition. The nitrates of copper offer an example of this kind of displacement.

Nitric acid of specific gravity 1.42 (which may be distilled without undergoing change) consists of 1 equivalent of the protohydrate with 3 equivalents of water, which correspond to the water of crystallization in a salt ( $\text{HO}$ ,  $\text{NO}_5$ , 3aq).—Nitrate of copper contains an equal number of equivalents of water of crystallization,  $\text{CuO}$ ,  $\text{NO}_5$ , 3aq. But there is also a subnitrate of copper, which represents

the nitrate of copper, in which the 3 equivalents of water of crystallization are displaced by 3 equivalents of hydrated oxide of copper,  $\text{CuO}$ ,  $\text{NO}_5$ , 3 ( $\text{CuO}$ ,  $\text{HO}$ ), a green compound which is left in the form of an insoluble powder, when the neutral nitrate of copper is partially decomposed by a heat of about  $400^\circ \text{F}$ .

Water may be displaced not only from saline combinations by metallic oxides, but may be removed from certain organic compounds by oxides which take its place. For example, a compound of sugar with oxide of lead,  $\text{C}_{12}\text{H}_{19}\text{O}_9 + 2 \text{PbO}$ , may be formed from cane sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , 2 aq) by boiling it with litharge, and on suspending this new compound in water, and removing the lead by means of sulphuretted hydrogen, the original quantity of water is restored, and the sugar is recovered with its characteristic properties;  $2 \text{HS} + \text{C}_{12}\text{H}_{19}\text{O}_9, 2 \text{PbO} = 2 \text{PbS} + (\text{C}_{12}\text{H}_{22}\text{O}_{11}, 2 \text{HO})$ .

The formation of many subsalts, however, is not explicable in this manner. Nitrate of lead, for example, crystallizes in anhydrous octohedra; but a crystallized dinitrate of lead may be obtained, consisting of ( $2 \text{PbO}$ ,  $\text{NO}_5 + 2 \text{aq}$ ); and a trisnitrate and hexanitrate of lead have also been obtained by Berzelius. In these cases the oxide of lead cannot be said to have taken the place of the water of crystallization of the neutral salt. All that can be said, is that in such cases the metallic oxide attaches itself to the neutral salt in a manner analogous to that in which water of crystallization does in other instances.

The tendency to the formation of subsalts is limited to certain acids and bases: sulphuric, nitric, carbonic and acetic acids, and the oxides of copper, of lead, of mercury, and of zinc, are the most remarkable in this respect.

(463) A class of compounds which resemble the subsalts more than any others, is presented to us in the bodies termed oxychlorides, oxyiodides, and oxycyanides. In these compounds, one equivalent of the chloride, of the iodide, or of the cyanide of a metal is united with one or more equivalents of the oxide of the same metal. Turner's yellow, which is an oxychloride of lead ( $\text{PbCl}$ , 7  $\text{PbO}$ ), is a well known commercial article belonging to this class. Such combinations usually occur in the case of chlorides or iodides which never form any but anhydrous crystals, and which consequently cannot be supposed to take up an oxide as a substitute for water of crystallization: any satisfactory theory of the class of subsalts must also account for the formation of compounds of this kind. There is, indeed, much in the chemical nature of such compounds that requires further investigation.

Some salts enter into combination with other bodies, and form compounds which are in many respects anomalous; such for instance are the compounds of ammonia with many dry salts: 2 equivalents of chloride of silver will in this manner absorb 3 equivalents of ammonia. Many of the salts of copper exhibit a similar power.

## CHAPTER XI.

### GROUP I.—METALS OF THE 'ALKALIES.

#### § I. POTASSIUM.

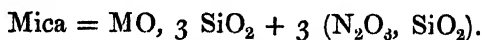
*Symbol K; Equivalent, 38.96; Specific Gravity, 0.865.*

*Native Compounds which contain Potash.*

Alum . . .	$\text{KO}, \text{SO}_3 + \text{Al}_2\text{O}_3, 3 \text{SO}_3 + 24 \text{ aq.}$
Felspar . . .	$(\text{K Na}) \text{O}, 3 \text{SiO}_2 + \text{Al}_2\text{O}_3, 3 \text{SiO}_2.$
Biaxal'mica . .	$\text{KO}, 3 \text{SiO}_2 + 3 [(\text{Al Fe})_2, \text{O}_3, \text{SiO}_2]$

(464) *Symbols of mixtures of Isomorphous Compounds.*—The formulæ employed above for felspar and mica require explanation, as the principle of notation adopted in these cases will be applied hereafter to the formulæ of a large number of minerals.

It often happens that isomorphous bases displace each other in the same mineral without altering its form or mineralogical characters, or even without altering its general chemical formula. Mica, for example, may be regarded as a compound of 1 equivalent of a silicate of a protoxide of a metal with 3 equivalents of a different silicate of a sesquioxide of a different metal. Let *m* stand for the metallic base of the protoxide, *n*, for the metallic base of the sesquioxide; the general formula for mica may then be expressed thus:—



Now the components of potash-mica are principally silicate of potash and silicate of alumina, the potash being the metallic protoxide and the alumina being the metallic sesquioxide; but sesquioxide of iron, sesquioxide of manganese, and sesquioxide of chrome, are also isomorphous with alumina, and these compounds frequently displace a portion of the alumina in combination; and this is especially the case

with the sesquioxide of iron. The peculiarity of isomorphous bases, when they displace each other, is this, that the displacement is liable to occur in any possible proportion; for example, in different specimens of mica the relative proportions of iron and aluminum are liable to great variations; indeed, they may vary indefinitely in amount, provided only that the quantity of the two metals taken together in any one specimen furnishes such a proportion of a metallic sesquioxide as is equivalent to the silica in that portion of the mineral: that is to say, that the two equivalents of metal required for combination with the 3 equivalents of oxygen in the sesquioxide, may either consist wholly of aluminum, or a *small but indefinite* proportion of the aluminum may have its place supplied by a *small but equivalent* quantity of iron, or a large proportion of the aluminum may have its place supplied by a corresponding and equivalent proportion of iron.

Now the method of notation adopted in the preceding formulæ is employed to indicate precisely this—that the proportions of the two or more metals, the symbols of which are bracketed together, thus,  $(\text{AlFeMn})_3\text{O}_{33}$ , are liable to vary within any conceivable limits, provided that the united amount of all the metals so bracketed be exactly sufficient to form a true sesquioxide with the three equivalents of oxygen.

In like manner in the case of the potash in felspar, part of the potassium may have its place supplied by sodium, or by calcium; but the proportions of the two taken together require exactly the same amount of oxygen, and consequently saturate the same proportion of silicic acid that 1 equivalent of potash alone would have required.

This frequent partial displacement of one isomorphous base by another in native crystallized minerals, renders much caution necessary in interpreting the results of an analysis. The difficulty of fixing the formula of a mineral of course increases with the complexity of its composition, and it is with the silicates especially that these difficulties are experienced. It is usual, when the analytical operations are completed, to ascertain the proportion of oxygen in the silicic acid, then the proportion of oxygen contained in the sesquioxides, and lastly the quantity of oxygen in the protoxides; because, however much the proportions of the different metals may vary in different specimens of the same mineral, the ratio of the oxygen in both sets of bases to the oxygen in the silicic acid remains uniform. In felspar, for instance, the proportion of oxygen in the silicic acid is 12, in the sesquioxide of

aluminum it is 3, and in the protoxide of potassium or sodium it is 1.

(465) POTASSIUM.—This remarkable metal was discovered by Sir H. Davy, in the year 1807, and its isolation marks an important era in the progress of philosophical chemistry. The alkalies and the earths had long been suspected to be compound bodies, but up to that period they had resisted all attempts to decompose them. When once potassium, however, had been separated from its compounds, and potash had been proved to be an oxide of this metal, the decomposition of  $\text{K}_2\text{O}$  other alkalies and earths followed as a necessary consequence: more correct ideas upon fundamental points of chemical theory were introduced; new methods of research were placed within reach of the analytical chemist, and potassium itself, from its powerful affinity for oxygen, became an important addition to the reagents of the laboratory.

*Properties.*—Potassium is a silver-white metal, which is brittle, and has a crystalline fracture at  $32^\circ \text{F.}$ ; at temperatures a little above this it is malleable; at  $60^\circ$  it is soft; as the temperature rises it becomes pasty, and at  $130^\circ$  it is completely liquid. Whilst in the soft condition, two clean surfaces of the metal admit of being welded together like iron; at a red heat it may be distilled, and it yields a beautiful green vapour. Potassium is light enough to float in water, having a specific gravity of only 0.865. If exposed to the air, even for a few minutes only, it becomes covered with a film of oxide: when heated to its point of volatilization it bursts into flame, and burns with great violence. The powerful attraction of potassium for oxygen is seen on throwing the metal into water, in which case part of the water is immediately decomposed; its oxygen combines with the potassium and forms potash, while the escaping hydrogen carries with it a small portion of the volatilized metal, and taking fire from the heat evolved, burns with a beautiful rose-red flame; the metal melts and swims about rapidly upon the water, and finally disappears with an explosive burst of steam, as the globule of melted potash which is formed by its oxidation becomes sufficiently cool to come into contact with the water. Potassium decomposes nearly all gases which contain oxygen, if it be heated in contact with them; and at a high temperature it will remove oxygen from almost all bodies into the constitution of which it enters. It becomes necessary therefore to preserve the metal either in exhausted hermetically sealed glass tubes, or under the surface of some liquid, like naphtha, which does not contain oxygen. At a heat short of redness potassium absorbs hydrogen, and becomes converted into a greyish mass. It likewise

absorbs carbonic oxide with facility when heated moderately in it, or when the vapour of potassium is allowed slowly to condense in an atmosphere of the gas, and a black mass is formed from which the metal cannot be recovered, and which often occasions considerable waste in the ordinary method of preparing potassium.

(466) *Preparation.*—Potassium was originally obtained by Sir H. Davy, by decomposing a fragment of hydrate of potash (which had become slightly moistened upon its surface by exposure to the air for a few minutes) by the current of a voltaic battery of 200 or 250 pairs of six-inch plates, on Wollaston's construction. The dry hydrate is an insulator, but a trace of moisture confers upon it a sufficient degree of conducting power: under such circumstances globules of metallic potassium separate at the negative wire, and may be preserved under naphtha. They burn vividly in air, leaving an intensely alkaline residue. This method of procuring the metal, however, furnishes it only in very small quantity, and is difficult and expensive.

Gay Lussac and Thénard, in 1808, invented a method by which potassium may be obtained by purely chemical means in greater abundance. Iron turnings were heated to whiteness in a curved gun-barrel, which was covered with a clay lute, to preserve it from the action of the air at a high temperature, and melted hydrate of potash was allowed slowly to pass over the ignited iron; decomposition ensued, the iron combined with the oxygen both of the potash and of the water, and potassium along with hydrogen passed forwards, the potassium condensing in a copper receiver which was kept cool.

The process, however, by which potassium is now obtained consists in decomposing the carbonate of potash by charcoal, a plan originally invented by M. Cuvraudau, and improved by Brunner. This operation has recently been carefully studied by MM. Donny and Mareska (*Ann. de Chimie*, III. xxxv. 144). In order to ensure a successful result, attention to a number of minute precautions is requisite. The material which is best adapted to this purpose is the potash salt of some vegetable acid, which, when decomposed by heat in a vessel from which air is excluded, leaves a large quantity of carbon. For this purpose the acid tartrate of potash, or crude tartar, is preferred. About six pounds of this substance is placed in a capacious iron crucible furnished with a cover, and ignited till it ceases to emit combustible vapours. A porous mass of carbonate of potash, intimately mixed with very finely divided carbon, is thus obtained: this is rapidly cooled by moistening the exterior of the crucible with cold water; the charcoal mass,

when cold, is broken up into lumps about the size of a hazel-nut, and quickly introduced into a wrought iron retort. This retort is usually made of one of the iron bottles in which mercury is imported; it is introduced into a furnace, *a*, as shown at *b*, fig. 288, and placed horizontally upon supports of fire brick, *ff*; a wrought

FIG. 288.

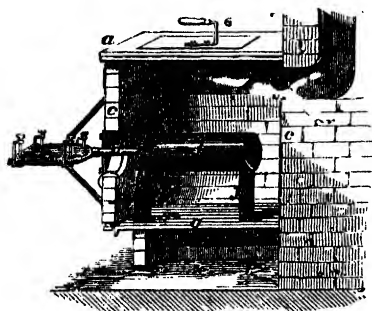
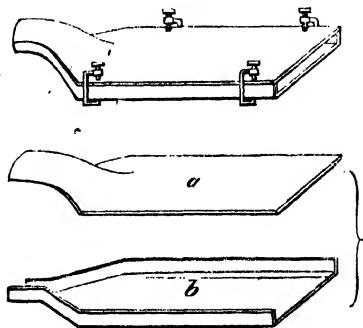


FIG. 289.



iron tube, *d*, four inches long, serves to convey the vapours of potassium produced during the distillation into a receiver, *e*, which it is found most advantageous to construct of the form shown separately in fig. 289. It consists of two pieces of wrought iron, *a*, *b*, which fit closely to each other, so as to form a shallow box only a quarter of an inch deep, and are confined in their places by clamp screws: the iron plate should be one-sixth of an inch thick, twelve inches long, and five inches wide; the receiver is open at both ends, the socket fitting upon the neck of the iron retort. The object of preparing the receiver of this particular form is to ensure the rapid cooling of the potassium, and so to withdraw it from the action of the carbonic oxide which is disengaged during the whole process. Before this receiver is connected with the tube, *d*, the fire is slowly raised until the retort attains a dull red heat; powdered vitrified borax is then sprinkled over its exterior; the borax melts, and forms a coating which protects the metal from oxidation. The heat is then urged until it becomes very intense. A mixture of coke and charcoal forms a fuel well adapted to this purpose; care should be taken that the temperature of the furnace be raised as equally throughout every part as possible. When a full reddish-white heat is attained, vapours of potassium begin to appear, and burn with a brilliant flame: the receiver is now adjusted to the iron neck of the retort, which is not allowed to project more than a quarter of an inch through the iron plate which forms part of the front wall, *c*, of the furnace, lest the tube should become

obstructed by the accumulation of solid potassium. Should any obstruction occur, it is removed by thrusting in an iron rod; if this fails, the fire must be immediately withdrawn; this is readily effected by removing the fire bars, *g*, from the furnace, with the exception of two which support the retort; the fuel thus falls into the ashpit. The receiver is kept cool by the application of a wet cloth upon its exterior. When the operation is complete, the receiver with the potassium is removed, and instantly plunged into a vessel of rectified Persian naphtha, provided with a cover. The vessel is kept cool by immersion in water. When this apparatus is sufficiently cold, the potassium is detached and preserved under naphtha.

In order to obtain the maximum produce of potassium, it is necessary that the mixture of carbonate of potash and carbon should contain 1 eq. of carbonate of potash to 2 of carbon, or 12 parts of carbon by weight to 69 of the carbonate. Upon the application of heat the mixture is wholly converted into carbonic oxide and potassium,  $\text{KO}, \text{CO}_2 + 2 \text{C} = \text{K} + 3 \text{CO}$ . The charge usually yields about one-fourth of its weight of crude potassium; some loss during the process is inevitable. MM. Donny and Mareska found this loss to amount to about one-third of the entire quantity contained in the charge.

The potassium so obtained is not pure; it is necessary to subject it to a second distillation in an iron retort. This precaution is *essential*, as if it be neglected a black detonating compound speedily forms by exposure to the atmosphere, and is even produced spontaneously, although the metal be kept under naphtha; this substance explodes violently upon the slightest friction. The purified metal amounts to about two-thirds of the quantity operated on. A third distillation may be necessary if the potassium be required in a state of perfect purity. In order to prevent the possibility of the formation of the detonating compound already mentioned, it is best to detach the tube from the retort as soon as it is cold, and to immerse it in water. A little impure potassium almost always remains in the tube, and is thus destroyed.

Potassium forms two compounds with oxygen: a protoxide,  $\text{KO}$ , which constitutes potash, and a teroxide,  $\text{KO}_3$ , which does not combine with acids.

(467) *Teroxide of Potassium*, ( $\text{KO}_3$ ); *Eq. 63*.—This substance is formed when potassium is burned in a silver spoon, or upon a mass of fused chloride of potassium in an excess of oxygen gas; a yellowish brown mass, fusible at a red heat, is thus obtained, as it



cools it assumes a scaly, crystalline texture. It parts readily with its excess of oxygen to combustibles, and is decomposed by water with extrication of oxygen and formation of a solution of pure potash, or protoxide of potassium.

(468) *Protoxide of Potassium; Potash, KO; Eq. 47.*—This compound can be procured in an anhydrous form by oxidating potassium in thin slices in air perfectly freed from moisture and carbonic acid. It is white, very deliquescent, and caustic; when moistened with water it becomes incandescent: after it has thus combined with water, no degree of heat is sufficient to expel the water. Anhydrous potash fuses at a red heat, and is volatilized at a high temperature. For most purposes the presence of water is immaterial, potash is therefore generally procured in the state of hydrate, in which form it may be obtained without difficulty.

*Hydrate of Potash, (KO, HO), Eq. 56, Sp. Gr. 2.2,* is prepared by dissolving carbonate of potash, of which pearlash of commerce is an impure variety, in ten or twelve times its weight of water, and adding to the boiling solution a quantity of quick lime equal in weight to half the carbonate of potash used; the lime should be slacked, and made into a thin paste with water, and added in small portions at a time, so that the liquid may be maintained at the boiling point: a crystalline carbonate of lime precipitates, and hydrate of potash remains in solution;  $KO, CO_2 + CaO, HO$  give  $KO, HO + CaO, CO_2$ . After decantation from the precipitate the liquid is rapidly evaporated in an iron or silver basin, till, when the heat is raised nearly to redness, it flows without ebullition, like oil; it is then either cast into cylinders in a metallic mould, or is poured upon a cold stone slab, and solidifies on cooling. Hydrate of potash may be obtained crystallized in acute rhombohedrons,  $HO, KO, 4 aq$ , from a hot concentrated aqueous solution.

Hydrate of potash is one of the most indispensable reagents to the chemist. It is therefore necessary that he should be able readily to ascertain its purity, and if needful prepare it for himself; for this purpose bicarbonate of potash, in crystals, may be decomposed in the manner above described by means of lime obtained from black marble. The impurities which occur most frequently in ordinary caustic potash are carbonic, sulphuric, hydrochloric, and silicic acids, lime, alumina, oxide of iron, and peroxide of potassium. When in a state of purity it is perfectly soluble in water without effervescence; a dilute solution gives no precipitate with baryta-water, showing the absence of carbonic and sulphuric acids; oxalate of ammonia, no precipitate, showing the absence of

lime. On neutralizing with nitric acid, nitrate of silver gives no precipitate, showing the absence of chlorine; freedom from iron or metallic impurities is shown by the absence of any precipitate on the addition of hydrosulphate of ammonia. Caustic potash, when pure, is wholly soluble in alcohol, the impurities above mentioned remaining undissolved. Common potash is therefore often purified by forming a solution of it in alcohol, and boiling down to dryness in a silver vessel, till it flows tranquilly; the alcohol is thus expelled, the melted hydrate is poured off upon a silver plate from the black crust which forms over its surface, and when cold, it is broken up and placed in a well closed bottle.

A solution of pure potash may also be readily obtained by Schubert's method, which consists in adding a hot solution of hydrate of baryta to a solution of sulphate of potash, until the liquid gives no further precipitate either with baryta or with the sulphate of potash;  $\text{KO}, \text{SO}_3 + \text{BaO}, \text{HO} = \text{KO}, \text{HO} + \text{BaO}, \text{SO}_3$ .

Hydrate of potash, after fusion, is a hard, greyish white substance; it rapidly absorbs moisture and carbonic acid from the air, dissolves in about half its weight of water, with the extrication of considerable heat, and it is soluble in alcohol to an almost equal extent. It has a peculiar nauseous odour, and a powerful acrid taste; is a powerful caustery, and quickly destroys both animal and vegetable matters; for this reason its solution cannot be filtered except through pounded glass or sand, and is always best clarified by allowing the impurities to subside, and then decanting the clear liquid.

The following table, by Dalton, gives approximatively the proportion of anhydrous potash contained in 100 parts by weight of solutions of the alkali of various densities:—

*Strength of Solutions of Potash.*

Sp. gr.	KO in 100 parts.	Sp. gr.	KO in 100 parts.
1'60	46'7	1'33	26'3
1'52	42'9	1'28	23'4
1'47	39'6	1'23	19'5
1'44	36'8	1'19	16'2
1'42	34'4	1'15	13'0
1'39	32'4	1'11	9'5
1'36	29'4	1'06	4'7

At a high temperature hydrate of potash is wholly volatilized, consequently the water cannot be expelled from this hydrate by the mere application of heat. Its affinities are so powerful that few vessels are found capable of resisting its action; those which contain

silica are decomposed by it, and platinum itself is oxidized when heated in contact with it. Gold and silver resist it better. Potash decomposes the fixed oils, and converts them into soluble soaps, and when fused with siliceous minerals it displaces the bases, and combines with the silica, forming silicate of potash. Potash is extensively employed in the arts; to the soap-boiler and the glass-maker it is indispensable; when combined with nitric acid, it enters largely into the manufacture of gunpowder, and in greater or less quantity it furnishes important aids to a variety of processes employed in the manufactures of the country. In the laboratory, potash is in constant use for separating the metallic oxides from solutions of their salts, as owing to the powerful affinity of the alkali for acids it readily decomposes all salts which are formed by metals which produce oxides insoluble in water. Potash is present in small proportion in all fertile soils, the grand reservoirs of this alkali being the different varieties of clay, which contain 2 or 3 per cent. of it derived from the disintegration of felspar, in which it is present in the proportion of from 10 to 12 per cent., and certain kinds of mica, which yield 5 or 6 per cent. By exposure to the air and atmospheric vicissitudes, these rocks become gradually disintegrated; their soluble constituents, potash amongst the number, are taken up by the water which falls upon the earth's surface, and are assimilated by the plants which spring from its bosom; they accumulate it, especially in the leaves, young shoots, and succulent parts. Owing to this circumstance large quantities of potash may be obtained with facility: dried brushwood is incinerated, and the remaining ash, which seldom constitutes more than 1 per cent. of the dry wood, contains the potash in the form of carbonate: the salt is extracted by water from the insoluble portions. In plants potash is usually combined with some organic acid; when the vegetable matter is burned, the acid is decomposed, carbonic acid is formed, and the alkali remains in the state of a carbonate in the ash.

(469) SULPHIDES OF POTASSIUM.—Potassium takes fire readily and burns with brilliancy when heated in the vapour of sulphur. It combines with this element in not less than five different proportions,  $KS$ ,  $KS_2$ ,  $KS_3$ ,  $KS_4$ , and  $KS_5$ . Owing to this circumstance, the reactions which occur when sulphur is heated with potash are somewhat complicated; but they are now well understood, and may be traced without difficulty. The *protosulphide*,  $KS$ , is easily procured by heating sulphate of potash in a current of hydrogen gas;  $KO, SO_3 + 4 H = KS + 4 HO$ : water is formed, and the sulphide, of a yellowish brown colour, is left behind in a fused

condition. If sulphate of potash be mixed in fine powder with half its weight of lampblack, and heated in a covered crucible, the sulphate is reduced to sulphide of potassium, which remains in a finely divided state mixed with the excess of charcoal, and yields a *pyrophorus*, or compound which takes fire spontaneously in the air, owing to the heat emitted by its rapid absorption of oxygen. Protosulphide of potassium deliquesces when exposed to the air; it dissolves in water, and when pure, forms a colourless solution which acts rapidly on the skin as a caustic. This solution, on the addition of an acid, evolves sulphuretted hydrogen abundantly;  $\text{KS} + \text{HO}, \text{SO}_3 = \text{HS} + \text{KO}, \text{SO}_3$ . It absorbs oxygen quickly from the air and becomes yellow. In solution it may be prepared by dividing a solution of caustic potash into two equal portions; and transmitting through one of them a current of sulphuretted hydrogen as long as it is absorbed; a hydrosulphate of sulphide of potassium is formed,  $(\text{KS}, \text{HS})$  and on mixing it with the other half of the potash ley, neutral sulphide is formed:  $\text{KS}, \text{HS} + \text{KO} = 2 \text{KS} + \text{HO}$ . The *bisulphide*,  $(\text{KS}_2)$ , may be formed by exposing an alcoholic solution of  $\text{KS}, \text{HS}$  to the air till it begins to become turbid, and evaporating to dryness *in vacuo*. It fuses easily, and is of an orange colour. The *tersulphide*,  $\text{KS}_3$ , is obtained pure by passing over ignited carbonate of potash the vapour of bisulphide of carbon as long as any gas makes its escape: carbonic acid and carbonic oxide are produced as follows;  $2 (\text{KO}, \text{CO}_2) + 3 \text{CS}_2 = 2 \text{KS}_3 + 4 \text{CO} + \text{CO}_2$ . In the old process of making liver of sulphur, 69 parts of dry carbonate of potash are fused with 40 parts of sulphur; the resulting yellowish brown mass consists of 3 eqs. of tersulphide of potassium and 1 of sulphate of potash: the potash, in this case yields oxygen to one portion of the sulphur, and forms sulphuric acid, as shown in the annexed equation:  $4 (\text{KO}, \text{CO}_2) + 10 \text{S} = (\text{KO}, \text{SO}_3 + 3 \text{KS}_3) + 4 \text{CO}_2$ . A *tetrasulphide*,  $\text{KS}_4$ , may be formed by reducing sulphate of potash by the vapour of bisulphide of carbon. The *pentasulphide*,  $\text{KS}_5$ , is formed by boiling a solution of any of the preceding sulphides with excess of sulphur till saturated, or by fusing any of the dry sulphides with an excess of sulphur; the excess of sulphur separates and floats above the sulphide, which has a dark-liver brown colour; it is deliquescent, and soluble in water. All these sulphides have an alkaline reaction to test paper, and a more or less distinct odour of sulphuretted hydrogen. On the addition of a stronger acid they are decomposed with extrication of sulphuretted hydrogen, attended, in the case of all but the protosulphide, by the precipitation of white finely divided

sulphur. On adding the persulphide to hydrochloric acid of sp. gr. about 1.1, the persulphide of hydrogen separates as an oily liquid. By exposing the higher sulphides to air, hyposulphite of potash forms in the solution, and the excess of sulphur separates. When a solution of caustic potash is boiled with sulphur, a decomposition ensues similar to that which occurs when potash and sulphur are fused together; a deep red liquid is formed, which contains hyposulphite of potash, and one of the higher sulphides of the metal: 3 equivalents of potash and 12 of sulphur would thus furnish 1 equivalent of hyposulphite and 2 equivalents of pentasulphide of potassium;  $3 \text{ KO} + 12 \text{ S} = \text{KO}, \text{S}_2\text{O}_2 + 2 \text{ KS}_5$ .

(470) *Chloride of Potassium*, (KCl); *Eq.* 74.5; *Sp. Gr.* 1.900.—This salt is extracted in considerable quantity from *kelp*, the ashes of burnt sea-weed, and is used largely as a source of potash in the manufacture of alum. It may be prepared pure by directly neutralizing bicarbonate or carbonate of potash with hydrochloric acid, and evaporating. It crystallizes in cubes, and dissolves very readily in cold water, which takes up about a third of its weight, attended with great depression of temperature. It is remarkable that this salt possesses the property of absorbing the vapours of anhydrous sulphuric acid, forming a hard, translucent mass, (KCl, 2 SO<sub>3</sub>), which is instantly decomposed by water. With chromic acid it forms a corresponding compound, which crystallizes from its solution in hydrochloric acid in needles (KCl, 2 CrO<sub>3</sub>).

(471) *Iodide of Potassium, or Hydriodate of Potash*, (KI); *Eq.* 166; *Sp. Gr.* 3.059.—This valuable medicine may be procured in several ways. A simple method consists in adding iodine to a solution of potash, gently warmed, until the solution begins to assume a brown tint. Iodide of potassium and iodate of potash are formed;  $6 \text{ I} + 6 \text{ KO} = 5 \text{ KI} + \text{KO}, \text{IO}_5$ . By gentle ignition of the residue obtained by evaporation, the iodate is decomposed, and the remaining iodide fuses. The salt must not be strongly heated, as iodide of potassium volatilizes at a red heat. A better plan is to digest 2 parts of iodine and 1 of iron, in a stoppered vessel, with 10 parts of water, the iron being purposely added in excess; under these circumstances protiodide of iron is formed by the direct union of the metal with the iodine: the liquid is then boiled, and a solution of carbonate of potash is added in small quantities as long as a precipitate occurs; the solution is next filtered from the insoluble carbonate of iron, and on evaporation it yields crystals of iodide of potassium;  $\text{FeI} + \text{KO}, \text{CO}_2 = \text{FeO}, \text{CO}_2 + \text{KI}$ . Iodide of potassium crystallizes in anhydrous cubes, which in a

dry air are not deliquescent. It is very soluble both in water and in alcohol, and has a cooling, bitterish taste. Its solution has the property of dissolving an additional equivalent of iodine, with which it forms a deep brown liquid.

Iodide of potassium, from its high price, has frequently been adulterated. If pure it should dissolve completely in six times its weight of alcohol, and should not effervesce when moistened with hydrochloric acid (carbonate of potash would be indicated by effervescence), and it should not turn brown by the action of the acid; if iodate of potash were mixed with it, free iodine would be shown by the brown colour developed on adding the acid.

(472) *Bromide of Potassium*, (KBr); *Eq.* 119; *Sp. Gr.* 2.672.—This is a very soluble salt, which crystallizes in cubes. It may be obtained by adding bromine to a solution of caustic potash until the liquid acquires a slight, permanent yellow colour. Bromide of potassium and bromate of potash are formed. Löwig dissolves the mixed salts in water, decomposes the bromate by a current of sulphuretted hydrogen, warms gently to expel the excess of the gas, filters from the deposited sulphur, and evaporates till the solution crystallizes;  $\text{KO}, \text{BrO}_3 + 6 \text{HS} = \text{KBr} + 6 \text{HIO} + 6 \text{S}$ .

(473) *Silicofluoride of Potassium*, ( $\text{KF}, \text{SiF}_2$ ); *Eq.* 110.3.—This salt is one of the most insoluble compounds of potassium; it falls as a transparent gelatinous precipitate whenever silicofluoric acid is added to a salt of potash; it dries to a white earthy-looking powder. Advantage is occasionally taken of its insolubility to separate potash from some of the acids with which it is united: in this way chloric acid is sometimes prepared from chlorate of potash.

(474) *Sulphate of Potash*, ( $\text{KO}, \text{SO}_3$ ); *Eq.* 87; *Sp. Gr.* 2.64.—This is a salt which crystallizes either in anhydrous six-sided prisms, terminating in six-sided pyramids, or in four-sided oblique rhombic prisms, which require about 16 parts of cold water for solution. The crystals decrepitate strongly when heated. Sulphate of potash forms a series of double salts with sulphates of the protoxides which are isomorphous with magnesia, and another class of salts (the varieties of alum) with the sulphates of the sesquioxides isomorphous with alumina. M. Jacquelin finds that if neutral sulphate of potash be dissolved in nitric acid, a little nitre and bisulphate of potash are formed, whilst a salt, consisting of  $\text{HIO}, \text{NO}_5 + 2(\text{KO}, \text{SO}_3)$ , crystallizes in oblique prisms. An analogous compound may be formed with phosphoric acid,  $3 \text{HO}, \text{PO}_5 + 2(\text{KO}, \text{SO}_3)$ .

*Bisulphate of Potash*, ( $\text{KO}, \text{SO}_3 + \text{HIO}, \text{SO}_3$ ); *Eq.* 136;

*Sp. Gr.* 2.475.—This salt is formed on a large scale as a residuary product in the preparation of nitric acid from nitrate of potash; it is the *sal enitrum* of the older writers. It crystallizes from a strongly acid solution in rhomboidal tables, which fuse at a heat below redness, and by prolonged ignition lose half their acid; they are very soluble in water, and have a sour bitterish taste. If redissolved in water, the neutral sulphate crystallizes first, and afterwards, when the liquid has become strongly acid, the bisulphate is deposited. The bisulphate occasionally crystallizes in anhydrous needles. This salt is sometimes used as a flux in cases where the action of an acid is required at a high temperature upon salts or metallic oxides with which it may be fused.

(475) *Nitrate of Potash*, ( $\text{KO}, \text{NO}_3$ ); *Eq.* 101; *Sp. Gr.* 2.070.—*Saltpetre* or *Nitre* as this salt is frequently termed, is one of the most important and valuable salts of potash. The principal supply of nitre is derived from various districts in the East Indies, where it occurs sometimes as an efflorescence upon the soil, at other times disseminated through the superficial stratum itself. It is obtained by lixiviating the soil, and allowing the solution to crystallize. The earth which furnishes it consists principally of loose, porous carbonate of lime, mixed with decomposing felspar, and it always contains more or less of organic matters. Notwithstanding the investigations of Pr. Davy, of M. Kuhlmann, and of others, the process of nitrification is still very imperfectly understood. The artificial formation of nitre has, however, been practised with considerable success in various countries of Europe, which furnish annually a large amount of the salt. In Sweden, this supply of nitre is considered of such importance, that each landed proprietor is obliged to pay a certain tax in raw nitre, the quantity required being proportioned to the value of the estate. Where animal matters are present in abundance, the formation of nitric acid is chiefly due to the gradual oxidation of ammonia developed in the process of putrefaction. This oxidation is materially favoured by an excess of potash, of lime, or of some basic substance, which can combine with the acid at the moment of its generation. The process of nitrification becomes arrested if the temperature be allowed to fall much below  $60^\circ \text{F}$ .

The method adopted in the artificial production of nitre consists in placing animal matters, mingled with ashes and lime rubbish, in loosely aggregated heaps, exposed to the air, but sheltered from rain. The heaps are watered from time to time with urine or stable runnings; at suitable intervals the earth is lixiviated, and

the salt crystallized. Three years usually elapse before the nitre bed is washed: after this interval a cubic foot of the *debris* should yield between four and five ounces of nitre. As there is always a considerable quantity of the nitrates of lime and magnesia present, which will not crystallize, carbonate of potash, in the shape of wood ashes, is added so long as any precipitate occurs. The nitrate of lime is decomposed, and the insoluble carbonate of lime separates;  $\text{CaO}, \text{NO}_3 + \text{KO}, \text{CO}_2 = \text{CaO}, \text{CO}_2 + \text{KO}, \text{NO}_3$ . The clear liquor is then evaporated and crystallized. It is found by the saltpetre-boiler that the earth in which nitre has once been formed furnishes fresh nitre more readily than on the first occasion. Care is taken that the nitre plantations, as they are termed, shall rest upon an impervious flooring of clay, so that the liquid which drains away from them may be collected and preserved.

In Prussia, by a more methodical treatment, a cubic foot of the earth yields about twenty ounces of nitre. The heaps are so constructed as to form a terrace of steps, exposing the back in the form of an upright wall to the prevailing wind; the watering is thus facilitated, while upon the exposed side the evaporation proceeds with rapidity, and here, from capillary action, the nitre chiefly accumulates: from time to time a layer of earth is removed from this wall for lixiviation, and the washed earth, mixed with a fresh portion of animal matter, is returned systematically to the other side of the heap.

The washing of the earth charged with saltpetre is conducted in a systematic manner, so as to avoid using a larger quantity of water than is actually needed to dissolve the saltpetre. The operation is minutely described by Regnault (*Cours Élémentaire de Chimie*, ii. 131).

Besides the natural and artificial sources of nitre just described, this salt occurs also in solution in the sap of certain plants, among which the sunflower, the tobacco plant, and common borage may be enumerated:

*Properties.*—Nitre crystallizes in long six-sided striated prisms, terminated by dihedral summits; it is soluble in three-and-a-half times its weight of cold water, and about half its weight of boiling water; it is insoluble in alcohol: its taste is cooling and saline. If paper be dipped in a solution of nitre and dried, it forms what is well known as *touch-paper*, which, when once kindled, steadily smoulders away till consumed, and hence it is largely employed in firing trains of powder, fireworks, &c. Nitre fuses easily without decomposition at a temperature of  $642^\circ \text{F.}$  (Person), and when cast



into moulds, solidifies to a white, fibrous, radiated mass, known as *sal prunelle*. Heated to redness, part of its oxygen is expelled, and a deliquescent mass of hyponitrite of potash is formed. By a still stronger heat the hyponitrite is decomposed, nitrogen mixed with oxygen escapes, and a mixture of potash and peroxide of potassium remains.

Owing to the facility with which nitre parts with oxygen, it is a powerful oxidating agent, and is in frequent demand in the laboratory for this purpose: when thrown upon glowing coals it produces a brisk scintillation. If intimately mixed with any metallic sulphide in fine powder, such as sulphide of antimony, and thrown, in small quantities at a time, into a red-hot crucible, the sulphur burns into sulphuric acid, which combines with the potash of the nitre with a brisk *deflagration*, or rapid combustion, whilst the metal at the same time becomes oxidized to the maximum. In the case of antimony, the oxide produced possesses acid characters, and it enters into combination with the potash. Advantage is frequently taken of this oxidizing action of nitre in order to convert small quantities of sulphur in bodies of organic origin into sulphuric acid, for the purpose of estimating the proportion of sulphur which they contain. The quantity of sulphuric acid thus produced, admits of easy and accurate determination in the form of sulphate of baryta.

(476) *Refining of Saltpetre*.—The impurities of most frequent occurrence in nitre are sulphate of potash, chloride of sodium, and nitrates of lime and magnesia: after it has been fused, unless the heat has been cautiously regulated, a little hyponitrite of potash is liable to be formed; in the latter case a fragment of the salt, when moistened with solution of sulphate of copper, becomes of a bright green colour. Nitre, when pure, is not deliquescent, and its solution gives no precipitate with solutions of chloride of barium, of nitrate of silver, or of carbonate of potash.

In the refining of nitre advantage is taken of the circumstance that whilst the solubility of nitrate of potash rapidly increases as the temperature rises, that of the chloride of sodium is scarcely affected by it. In England it is usual to purify the salt by three successive crystallizations. The same object is effected in France by a single operation. The following is an outline of the French process of refining saltpetre:—In a capacious copper boiler, about fifty gallons, or 500 pounds of water is placed, and twice its weight of crude nitre is added: this salt gradually dissolves, and fresh nitre is added until, when the water has attained the boiling point,

a quantity of nitre has been added equal to five times the weight of the water employed; the liquid is skimmed from time to time, and the chloride of sodium, a large proportion of which remains undissolved, is removed by means of perforated ladles; the solution is next diluted with 100 gallons of water, after which two pounds and a half of glue, dissolved in hot water, are added, and thoroughly incorporated by briskly stirring; the coagulum which is formed rises in a scum to the surface, and is carefully removed; when the liquid has been rendered clear by a few minutes' ebullition, it is allowed to cool to about  $195^{\circ}$ , and is ladled into the crystallizing pan.

The crystallization is effected in a shallow vessel, the bottom of which is formed by two inclined planes which meet in the middle. In this vessel the solution is kept in continual agitation, in order to prevent the formation of large crystals: such crystals would mechanically retain the mother-liquor, from which they could not be subsequently freed without recrystallization. The chloride of sodium, being nearly as soluble in cold water as in hot, remains almost entirely in the solution, whilst the saltpetre is deposited in extremely small crystals, which are allowed to drain, and are then removed to tanks provided with false, perforated bottoms, where they are deprived of the mother-liquor with which they are saturated. For this purpose the tanks are completely filled with the crystals, and upon them is poured a solution of saltpetre saturated in the cold; this liquid dissolves the chlorides, but leaves the pure nitrate of potash untouched. In the course of a few hours the liquid is drawn off, and the tanks are then filled up with pure water; this becomes charged with nitre, containing traces of chlorides, whilst the undissolved salt is almost chemically pure: the solution of nitre thus obtained serves to wash a fresh portion of the crystals: the refined saltpetre is then dried, and is fit for use.

(477) *Gunpowder*.—The principal consumption of nitre is in the manufacture of gunpowder, which consists of an intimate mechanical mixture of nitre, sulphur, and charcoal, in proportions approaching to 1 equivalent each of nitre and of sulphur, and 3 equivalents of charcoal.

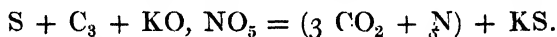
				In 100 parts.			
Nitre	.	.	1 eq. 101	.	.	.	74.8
Sulphur	.	.	1 eq. 16	.	.	.	13.3
Charcoal	.	.	3 eq. 18	.	.	.	11.9
				<hr/>			
				135			
				<hr/>			
				100.0			

The proportions used vary a little in different countries, as will be seen from the following table:—

*Composition of Gunpowder in 100 parts.*

	English and Austrian.	Prussian.	Swedish.	Chinese.	French.		
Nitre	75	75	75	75.7	75.0	76.9	62
Sulphur	10	11.5	9	9.9	12.5	9.6	20
Charcoal	15	13.5	16	14.4	12.5	13.5	18
	Musket.	Musket.	Musket.		Musket.	Sporting.	Blasting.

An excess of sulphur is carefully avoided on account of its injurious action upon the metal of the gun. The great explosive power of gunpowder is due to the sudden development of a large volume of nitrogen and carbonic acid gases, which, at the ordinary temperature of the air, would occupy a space equal to about 300 times the bulk of the powder used, but from the intense heat developed at the moment of the explosion, the dilatation amounts to at least 1500 times the volume of the gunpowder employed. Supposing the mixture to contain 1 equivalent of sulphur, 3 of carbon, and 1 of nitre, the reaction may be approximatively represented thus,



The only solid residue therefore is sulphide of potassium; and it is this substance which gives the peculiar sulphurous odour to the washings of a gun barrel.

Much care is requisite in the selection of the materials for the manufacture of gunpowder. The charcoal must be burned thoroughly, but not at too high a temperature: that from the alder or dog-wood is preferred for the purpose. In the government works at Waltham Abbey, sulphur is never used in the state of flowers of sulphur; in this condition it is preferred for fireworks; but distilled sulphur, reduced to a fine meal by grinding, is always used for gunpowder. Nitre of the purest quality is alone employed. These three materials having been separately ground and sifted, are mixed in powder in the proper proportions, and are intimately blended in a revolving drum; they are then made into a stiff paste with water, and ground for some hours under edge stones; the slightly coherent mass thus procured is broken up, and spread, in layers of about an inch in thickness, between gun-metal plates; it is then subjected to the action of a hydraulic press which exerts a force of 120 tons upon the square foot; a hard, sonorous mass, termed *press cake*, is thus obtained: these masses, whilst still damp, are broken into small fragments, or *granulated*, by submitting them to the action of toothed rollers in a machine con-

structed for the purpose. The grains are next sorted by means of sieves into different sizes, after which they are thoroughly dried in closets heated by steam, and, finally, are polished by placing them in barrels caused to revolve about thirty-nine times in a minute. A cubic foot of good English cannon powder weighs about fifty-eight pounds; if below fifty-five pounds, it is considered unfit for use. The heavier the powder the greater is its explosive power. Two ounces of the best English powder, when introduced into a mortar of eight inches diameter, set at an angle of  $45^\circ$ , should throw a 68lb. shot from 260 to 280 feet, on level ground.

The object of granulating the powder is to favour the rapidity of inflammation by leaving interstices, through which the flame is enabled to penetrate and envelope each grain. The ignition of the whole charge does not take place simultaneously throughout, nor is it desirable that it should do so, otherwise sufficient time would not be given to allow the charge to receive the full advantage of the expansive force of the air generated: too rapid an action would be expended upon the barrel of the gun itself, and effects would be produced like those due to fulminating mercury; indeed, where very great force is required, as in blasting for mining operations, the action of the powder is still further retarded by mixing it with sawdust; the powder for this purpose usually contains 65 parts of nitre, 20 of sulphur, and 15 of charcoal (Graham). In the formation of the fuse, the quick and slow match, and certain kinds of fireworks, gunpowder is mingled with combustibles in various proportions.

The analysis of gunpowder is easily effected: 100 grains of the powder for examination are dried at  $212^\circ$  by a steam bath; the loss indicates the amount of moisture. The residue is digested in water and is washed: the solution, when evaporated in a counterpoised capsule, and weighed, furnishes the amount of nitre, and other salts. Nitrate of baryta, when added to a solution of these salts, acidulated with nitric acid, will yield the sulphuric acid in the form of sulphate of baryta; and nitrate of silver, when added to the liquid filtered from the sulphate of baryta, will give the data for ascertaining the amount of chloride from the precipitated chloride of silver: the charcoal and sulphur are contained in the portion which did not dissolve in water; they may be separated by means of bisulphide of carbon, which dissolves out the sulphur, and leaves it in the crystalline form by spontaneous evaporation, whilst the charcoal is left undissolved and may be weighed.

. A mixture of 3 parts of nitre, 2 of carbonate of potash. and 1

of sulphur, produces a compound known as *pulvis fulminans*, which when heated on an iron shovel until fusion takes place, suddenly explodes with a very loud report.

(478) *Chlorate of Potash*, ( $\text{KO}, \text{ClO}_3$ ); *Eq.* 122.5; *Sp. Gr.* 1.989.—One mode of preparing this salt has already been explained (321). It may be more economically prepared by exposing to a current of chlorine gas a mixture, in a slightly damp state, of 69 parts of carbonate of potash and 168 parts of caustic lime, previously reduced to the state of hydrate; chlorate of potash, carbonate of lime, and chloride of calcium are formed: boiling water dissolves both the chlorate of potash and the chloride of calcium. The two salts are easily separated by crystallization; as the chlorate requires 16 parts of cold water for solution, and the chloride is soluble to almost any extent. The chlorate of potash is deposited in anhydrous, rhomboidal, pearly tables; it has a cooling taste, somewhat analogous to that of nitre: 100 parts of boiling water dissolve 61.5 of the salt. When heated to redness the salt melts and is decomposed, furnishing oxygen gas of great purity, and leaving chloride of potassium as a fixed residue behind. It is a more powerful oxidizing agent than nitre; and if combustible substances, such as sulphur or phosphorus, be rubbed with it forcibly, combination with oxygen, accompanied by detonation, ensues. Chlorate of potash is principally consumed in the manufacture of lucifer matches, and as an oxidizing agent in certain operations of the calico printer. The preparation and properties of *perchlorate of potash* have been already described (322).

(479) *Carbonate of Potash*, ( $\text{KO}, \text{CO}_2$ ); *Eq.* 69; *Sp. Gr.* 2.103.—This important salt is obtained in large quantities for commercial purposes by lixiviating wood ashes and evaporating the solution until it crystallizes; the mother-liquor, when it cools, is poured off from the crystallized salts, as it retains the more soluble carbonate of potash, and when evaporated to dryness, affords the *potashes* of commerce, and these, when calcined, yield the impure carbonate known as *pearlash*. Different plants, when burned, furnish varying quantities of the alkali, which they extract from the soil: the leaves and young shoots, where the vital action is the most vigorous, are the parts which furnish the greatest quantity of alkali. Herbaceous plants, therefore, generally furnish more than shrubs, and shrubs more than an equal weight of timber. In the wine producing countries, a considerable quantity of carbonate of potash of good quality is furnished by burning the refuse yeast after the fermentation is complete. The yeast, for this purpose, is pressed, dried in the sun, and burned in shallow enclosures: this dry

matter furnishes nearly 10 per cent. of its weight of carbonate. Potash does not exist in plants in the form of carbonate; it occurs in them in union with different organic acids: these organic acids are destroyed by the action of the heat during incineration. These acids always contain more carbon than is sufficient, when oxidized by the air, to form the amount of carbonic acid requisite to neutralize the potash; and the carbonate of potash thus produced, as it is not decomposed by a red heat, remains behind. In the ashes of plants various other saline substances are likewise present, but those which are soluble consist principally of the sulphate of potash and chloride of potassium.

A purer carbonate is obtained for chemical purposes by deflagrating a mixture of purified cream of tartar with an equal quantity of pure nitre. The mass is thrown, in small portions at a time, into a red-hot crucible: in this operation the nitre yields oxygen to the vegetable acid, converts the carbon which it contains into carbonic acid, which enters into combination with the alkali both of the tartar and of the nitre, since the two acids undergo mutual decomposition: by lixiviation the carbonate of potash is extracted from the dry mass.

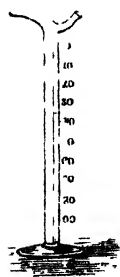
Carbonate of potash is a deliquescent salt, which is with difficulty obtained in oblique rhombic octohedral crystals, with 2 equivalents of water. Its reaction upon test paper is strongly alkaline; it has an acrid, alkaline taste. Its solutions have a peculiar lixivial smell: 100 parts of water at 60° dissolve 90 of carbonate of potash; and at the boiling point take up 205 parts, or rather more than twice their weight, of the salt. Alcohol does not dissolve it. Carbonate of potash fuses by exposure to a red heat, and at a very high temperature is partially volatilized; at a red heat it is decomposed by silica, carbonic acid is expelled with effervescence, whilst the silica, uniting with the alkali, forms with it a true silicate, the basis of one of the varieties of glass. Advantage is taken of this property in the analysis of mineral substances which contain a large quantity of silica, and which are not easily decomposed by the action of acids. For this purpose the mineral to be analysed is reduced to an extremely fine powder by careful levigation; a portion of this powder is accurately weighed, and then intimately mixed with about 3 times its weight of carbonate of potash, or, still better, with 3 parts of a mixture of 5½ parts of dried carbonate of soda and 7 parts of carbonate of potash; the whole is introduced into a platinum crucible, and exposed to a bright red heat for an hour. The mass enters into fusion, carbonic acid escapes

with effervescence, and a silicate of potash is formed, by which means all the bases of the mineral, which before were combined with the silica, are set at liberty. Upon now treating the mass with dilute hydrochloric acid, the silicate of potash is decomposed, the earths and metallic oxides are dissolved, and the silica partially dissolves and partially separates in the hydrated form. In order to decompose the hydrate of silica, the solution is evaporated to dryness, and again treated with acidulated water; the whole is now placed upon a filter, and the silica, after being well washed, remains behind in a state of purity. The analysis of the filtered liquid is then finished according to the ordinary method adopted for substances directly soluble in acids.

(480) *Alkalimetry*.—Since the quantity of alkaline carbonate is liable to great variations in different samples of the ash; and since the commercial value of pearl-ash depends upon the amount of carbonate which it contains, a rapid and sufficiently accurate method of analysis of this salt becomes a desideratum. In order to effect this object, the process termed alkalimetry has been invented. In principle it depends upon the determination of the number of divisions of a diluted acid, of definite strength, which 100 grains of the different samples of ash are capable of neutralizing; the neutralization being estimated by the action of the solution upon blue litmus paper.

The acid solution which is to be employed is measured from a burette or *alkalimeter*, which is a tube of the form shown in fig. 290. It has an internal diameter of about five-eighths of an inch, and is sufficiently tall to contain rather more than 1000 grains of distilled water. The space occupied by 1000 grains of water at 60° is marked off and indicated as 0, and the tube is then subdivided into 100 equal parts, each capable of containing 10 grains of water: opposite every tenth division the number corresponding to it is placed, the numbers increasing from above downwards.

FIG. 290.



Various plans have been proposed for preparing the dilute acid; the following is substantially the same as that recommended by Dr. Faraday (*Chemical Manipulation*, third edition, p. 281). It has the advantage of being readily applicable to any alkali.

A solution of sulphuric acid is prepared by diluting the ordinary commercial acid with eight times its *bulk* of distilled water: when

cool the liquid, which may be termed *alkalimetric acid*, should have a specific gravity of 1.1268. In order to ascertain whether the strength of this alkalimetric acid be accurately adjusted, a quantity of crystallized bicarbonate of potash is fused in a platinum crucible in order to convert it into the carbonate: the fused mass is poured upon a clean iron plate, and 100 grains of it are quickly weighed, and dissolved in about 3 ounces of water in a small evaporating basin. The alkalimeter is filled up to the division 65 with the dilute acid, and then water is to be added until it stands at the mark 0: the acid and water are to be thoroughly mixed by closing the tube with the thumb and finger, then inverting and agitating the tube; after which the liquid is added to the solution of carbonate of potash, which is to be gently warmed in order to expel the carbonic acid as it is liberated. A piece of blue litmus paper is placed in the basin, and the acid is cautiously added until the litmus paper is distinctly but permanently reddened. The acid liquid, if properly diluted, ought to contain, in each division, sufficient sulphuric acid to neutralize 1 grain of carbonate of potash; and the entire contents of the alkalimeter should, therefore, exactly produce this effect. If more than 100 divisions of the acid be required, the test acid is too weak; if less than 100 divisions, it is too strong.

Suppose that 95 divisions of the acid were sufficient, the 95 parts should have occupied 100 of the original diluted acid, in consequence of the alkalimetric acid, from which it was prepared, containing one-twentieth too much acid. Each 95 measures of this acid, therefore, must be diluted with 5 measures of water. If, on the other hand, more acid than 100 divisions be required, say 105 be needed, the acid contains one-twentieth too much water; the 35 divisions of alkalimetric acid used in the experiment require the addition of one-twentieth more of acid than they originally contained, this one-twentieth part is 1.75, but only one-fifth of this is acid, so that 0.25 parts by *weight* of the oil of vitriol originally used, must be added to each 35 parts by weight of alkalimetric acid. This correction, though not mathematically exact, is perfectly sufficient for all practical purposes. The alkalimetric acid, when duly adjusted, is preserved in bottles which are accurately closed.

Having thus prepared a test acid of the proper strength, 100 grains of the sample of pearlash for trial is dissolved in 3 or 4 ounces of water, filtered if necessary, and then tested in the same manner: the number of divisions of acid consumed will



indicate the per-centage of carbonate of potash present in the sample.

The same acid may be employed to determine the quantity of soda present in any sample of soda-ash; but as a certain weight of soda neutralizes a proportionately larger amount of acid than an equal weight of potash, the alkalimeter must be filled to a higher mark with the acid. For the determination of the quantity of pure potash in any sample, the acid must be filled to the division 49, and the tube must be then filled up to 0 with water. Each division will then contain acid sufficient to neutralize 1 grain of caustic potash.

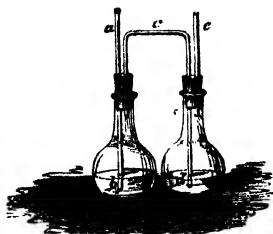
If filled to 65, then filled up with water, each division will correspond to 1 grain of carbonate of potash.

If filled to 54.6, and then filled up with water, each division will indicate 1 grain of dry carbonate of soda: and if filled to 23.4, and then water be added to 0, the acid in each division will neutralize 1 grain of caustic soda.

In estimating the value of soda-ash, which often contains sulphide of sodium, and hyposulphite of soda, an error might be occasioned by adopting this method, as both the sulphide of sodium and the hyposulphite of soda would be decomposed by the sulphuric acid, and would neutralize it, and thus would be reckoned as caustic soda.

The presence of caustic alkali in any sample is easily ascertained by the action of the solution upon nitrate of silver: the carbonates of the alkalis occasion a white precipitate of carbonate of silver; but if they contain any caustic alkali, a brown precipitate of hydrated oxide of silver is produced. The presence of sulphides in the ash is immediately manifested by the odour of sulphuretted hydrogen on neutralizing with an acid; if any sulphide be present, it will blacken the salts of silver, and interfere with its application as a test for caustic potash or soda.

FIG. 291.



(481) The proportion of carbonic acid in any sample of alkali is readily ascertained by means of the apparatus employed for the purpose by Will and Fresenius, represented in fig. 291: *b* is a light flask, of about 3 ounces capacity, in which 100 grains of the alkali are placed with about 1 ounce of water: *d* is a similar flask, in which about 1½ ounces by measure of oil of vitriol are placed. A sound cork is fitted into the neck of each flask, and is pierced with two

apertures for the reception of the tubes, *a*, *c*, and *e*, all of which are open at both ends: the tube, *a*, is sufficiently long to dip into the liquid in the flask; *c* is a bent tube, the longer limb of which passes into the acid in the flask, *d*. The outer extremity of *a* is closed, during the experiment, by a plug of wax or of soft cement. The apparatus is charged in the manner already described, and is accurately weighed after it has been connected together. A partial vacuum is now made by applying the mouth to the tube, *e*, and exhausting a portion of the air; the acid rises in the tube, *c*, and passes over into *b* to supply the place of the air which has been withdrawn; effervescence is occasioned by the escape of the carbonic acid, which passes off through the tube, *c*, and is dried as it bubbles up through the oil of vitriol in the flask, *d*. As soon as the effervescence has ceased, a fresh portion of acid is forced over from *d* into *b* by again partially exhausting the air: and this process is repeated until no further effervescence is occasioned by the fresh acid. The plug of wax is now withdrawn from the tube, *a*, and a current of air is forced through the apparatus by exhausting with the mouth at *e*, and the carbonic acid is thus completely displaced. The plug is now replaced in the tube, *a*, and the apparatus is weighed a second time. The difference between this weight and that obtained on the first occasion, indicates the amount of carbonic acid which has been expelled.

If any sulphide or sulphite of the alkali be present, the error which it might occasion by loss of sulphuretted hydrogen, or of sulphurous acid, in the gaseous state, and which would be reckoned as carbonic acid, is prevented by mixing from 20 to 30 grains of neutral chromate of potash with the sample under trial: the chromic acid which is liberated by the subsequent action of the sulphuric acid upon the chromate, imparts oxygen to the sulphuretted hydrogen or sulphurous acid, and converts both into sulphuric acid, which would be retained, and would in no way interfere with the result.

Carbonate of potash is largely consumed in the arts, as for example, in the manufacture of soap and of glass, and for preparing caustic potash and other compounds of potash. It also furnishes the chemist with one of his most indispensable reagents.

(482) *Bicarbonate of Potash*, ( $\text{HO, KO, 2 CO}_2$ ); *Eg.* 100; *Sp. Gr.* 2.052.—By passing a current of carbonic acid through a strong solution of the carbonate of potash, crystals of the bicarbonate are deposited in the form of right rhombic prisms; they are permanent in the air. The solution of the bicarbonate, if

exposed to the atmosphere, gradually loses one-fourth of its carbonic acid, forming a sesquicarbonate; and if boiled, the same change occurs much more quickly. The bicarbonate is converted into the neutral carbonate when fused by means of heat. The bicarbonate of potash has no alkaline reaction. It may be employed for procuring the compounds of potash in great purity, as, if well crystallized, it is almost absolutely pure, and may be obtained in this state with less difficulty than any other salt of potash. It is consumed medicinally in considerable quantities, for making effervescing draughts by the addition of citric or tartaric acid to its solution in water.

(483) CHARACTERS OF THE SALTS OF POTASH.—The salts of potash, with a colourless acid, are all colourless. They seldom contain any water of crystallization, yet many of them are deliquescent: the carbonate and acetate offer striking instances of this peculiarity, and furnish in this respect a marked contrast to the corresponding salts of soda. The salts of potash, when pure, if introduced upon a platinum wire into the reducing flame of the blowpipe, communicate to it a violet tint; the presence, however, of a small quantity of a salt of soda, masks this effect, in consequence of the strong yellow flame occasioned in similar circumstances by the compounds of soda. The presence of potash in solution is recognised, after the absence of everything but soda has been ascertained, by the following characters. 1. If moderately concentrated, a solution of *tartaric acid* in excess causes, upon brisk stirring, a white crystalline precipitate of bitartrate of potash, which is readily dissolved upon adding an alkali. 2 and 3. *Perchlorate* or *Carbazotate* of soda has also sometimes been employed as a test for potash, since both the perchloric and carbazotic acids form potash salts of sparing solubility. These compounds, however, are all soluble to a considerable extent in cold water, and unless tolerably strong solutions are employed they do not immediately subside. 4. With *silicofluoric acid* they yield a transparent gelatinous silicofluoride, which forms a white powder on drying. 5. The most conclusive reaction however, is produced with the *bichloride of platinum*; upon mixing a strong solution of this salt with a concentrated one of a salt of potash, a yellow double salt, consisting of  $(KCl, PtCl_2)$  separates in crystals; it is quite insoluble in alcohol and ether, but is slightly taken up by cold water. It is therefore best for analytical purposes to acidulate the solution suspected to contain potash with a little hydrochloric acid, and having added a slight excess of the solution of bichloride of platinum, to evaporate to dryness over the water

bath, and to wash the residue with Alcohol as long as anything is dissolved. This salt when heated to redness is decomposed, the platinum loses its chlorine, and the chloride of potassium may be dissolved out of the grey residue with cold water, whilst metallic platinum is left behind. 100 parts of the chloride of platinum and potassium are equivalent to 15.98 of potassium, or to 19.26 of potash.

## § II. SODIUM,

*Symbol, Na; Equivalent, 22.97; Specific Gravity, 0.972.*

(484) SODIUM may be obtained from carbonate of soda by a process analogous to that used for potassium. M. Deville recommends the employment of the following mixture in the preparation of sodium :—

Dried carbonate of soda . . . .	717 parts.
Powdered charcoal . . . . .	175 „
Finely powdered chalk . . . .	108 „

These materials are mixed intimately and kneaded into a stiff paste with oil, and calcined in a covered iron pot: the mass is then introduced into an iron retort and distilled, with the precautions described when speaking of potassium; it ought to yield nearly one-third of its weight of sodium: the object of adding the chalk is to prevent the charcoal from separating from the carbonate of soda when this salt fuses.

Sodium has a bluish white colour; in appearance and properties it much resembles potassium, but is somewhat more volatile; it fuses at a temperature of  $194^{\circ}$  F. When dropped into cold water it decomposes a portion of it, extricating hydrogen, but the gas does not take fire unless the water be heated previously.

The great storehouse of sodium is common salt, which is met with in nature in extensive deposits; it is also contained in vast quantities in the water of the ocean; the immense quantities of soda consumed in the arts are almost exclusively obtained from chloride of sodium, by a process presently to be described.

(485) *Oxide of Sodium*, or *Soda* ( $\text{NaO}$ , *Eq.* 31), forms the basis of the important series of salts of soda. It can be procured in an anhydrous state by burning the metal in dry air or oxygen gas; it is of a white colour, attracts moisture as greedily as the corresponding oxide of potassium, and this water cannot again be expelled from it by heat. In appearance and properties the hydrate exactly resembles that of potash, and may be formed by a similar method.

Dalton gives the following table of the proportion of anhydrous soda which is contained in solutions of soda of different densities :—

*Strength of Solutions of Soda.*

p. gr.	NaO in 100 parts.	Sp. gr.	NaO in 100 parts.
1'56	41'2	1'32	23'0
1'50	36'8	1'29	19'0
1'47	34'0	1'23	16'0
1'44	31'0	1'18	13'0
1'40	29'0	1'12	9'0
1'36	26'0	1'06	4'7

A *sesquioxide of sodium* ( $\text{Na}_2\text{O}_3$ ) appears also to exist.

The *sulphides* of sodium correspond in number with those of potassium, which they closely resemble. They may be prepared by analogous methods.

(486) *Chloride of Sodium*, ( $\text{NaCl}$ ); *Eq.* 58'5; *Sp. Gr.* 2'011.—This important and well known compound, formerly called *muriate of soda*, constitutes common culinary or table-salt. It is found native in the solid form, and it exists in solution in sea water in a proportion of about 2'7 per cent., which amounts to nearly 4 ounces per gallon, or to a bushel in from 300 to 350 gallons.

The extraction of the chloride from sea water was formerly practised to some extent upon the southern coast of our own island, but the manufacture is now unimportant, though in the southern countries of Europe the preparation of bay-salt is still a branch of industry of some magnitude. In conducting this process the sea water is allowed to run into shallow pools, the water evaporates and becomes concentrated by the heat of the sun: crusts of the salt form, and are raked off from time to time; the rough crystals thus obtained furnish the *bay-salt* of commerce. The concentrated sea water, or *bittern*, is employed as a source of bromine. Considerable quantities of magnesia are also extracted from it, as the chloride of magnesium, being deliquescent, remains in solution. M. Balard, who has devoted much attention to the study of these mother-liquors, has devised a method of extracting from them not only sulphate of magnesia and chloride of magnesium, but also an important quantity of potash, in the form of a double sulphate of potash and magnesia, as well as of a double chloride of potassium and magnesium. (Regnault, *Cours de Chimie*, ii. 192, &c.) The process requires a careful attention to the temperature at which the crystallizations are effected.

Immense beds of common salt are met with in Cheshire, in Poland at Wielitzka, and at Cardona in Spain. It has also recently been found in abundance near Belfast. Near Northwich, the principal deposit of rock salt in England, the mineral occurs in two beds, situated one above another, separated by about thirty feet of clay and marl intersected with small veins of salt: the two beds together are not less than sixty feet in thickness, 300 yards broad, and a mile and a half long. These beds occur in magnesian limestone. The celebrated and beautiful mine of Wielitzka contains sufficient salt to supply the entire world for ages. It is calculated that the mass of rock salt here is 500 miles in length, twenty miles broad, and not less than 1200 feet in thickness. This salt deposit occurs in the chalk formation. Chloride of sodium is sometimes found crystallized, and is then termed *sal gem*, or rock salt. The solubility of this chloride is frequently employed as a means of diminishing the labour of raising the salt to the surface, water being let down into the bed of salt and allowed to remain till it has become saturated: it is then pumped out, and the brine is boiled down and crystallized. Some brine springs contain too small a portion of salt to render it profitable to effect the evaporation by heat; the water in these cases is therefore concentrated by *graduation*, as at Salzburg: this process consists in exposing the brine, diffused over a large surface, to the air, by pumping it up to a height, and then allowing it to trickle slowly over large stacks of fagots, piled in suitable buildings, freely exposed to the prevailing wind: after this process has been repeated eight or ten times, the solution acquires a density of about 1.140, and is sufficiently concentrated to allow the evaporation to be finished as usual by the direct application of heat. In the first basin an insoluble double sulphate of lime and soda is deposited, partly in the form of mud, or *schlot*, as the Germans term it, partly in the form of a hard scale, which adheres to the bottom of the pan: when the liquor reaches a density of 1.236 it is decanted into another pan, and evaporated; the crusts of salt are removed as they form.

The appearance of the salt varies according to the rate at which the evaporation is conducted; when boiled down rapidly, it forms the mealy, fine-grained salt used upon our tables: if evaporated more slowly, the hard, crystallized salt preferred for fishery purposes is obtained. The salt of commerce always contains a certain proportion of chloride of magnesium, which gives it a slightly deliquescent character, and adds to the pungency of its flavour.

*Properties.*—Chloride of sodium has an agreeable saline taste.

It crystallizes in colourless transparent cubes, which are anhydrous, soluble in about 3 parts of cold water, and scarcely more soluble at a temperature of  $212^{\circ}$ . Water at  $32^{\circ}$  dissolves 35.5 per cent. of the salt, and at the boiling point of the solution, 41.2 per cent. When heated suddenly, the crystals decrepitate with violence; at a bright red heat they fuse, and by a stronger heat are converted into vapour. Chloride of sodium is insoluble in pure alcohol, but is taken up in considerable quantity by dilute spirit. By exposing its solution to a temperature of about  $14^{\circ}$  F., it crystallizes in hexagonal tables, which contain 4 or 6 equivalents of water: as the temperature rises, the water separates, the crystals fall to pieces, and they form a heap of minute cubes.

Chloride of sodium is consumed in large quantities in the manufacture of the salts of soda, and is daily an article of domestic use, being indeed an essential constituent of the food both of man and of animals, who languish if it be supplied in insufficient quantity. The process of salting meat is resorted to on account of the powerful antiseptic qualities of the chloride of sodium. In this operation a large quantity of the nutritive juices of the meat is extracted, which when saturated with the salt form the brine. Meat thus prepared is much less digestible and nutritious than fresh meat.

(487) *Iodide and bromide of sodium* crystallize in cubes, and are anhydrous: they may be procured by processes analogous to those used for the corresponding compounds of potassium; they occur native in sea-water in minute proportions, but small as these proportions are, they furnish the commercial supply both of bromine and of iodine. The iodine, though still less abundant than the bromine, is obtained with greater facility, as many marine plants appropriate it to their nutrition, and by burning them, it remains in the residue: the ash thus obtained goes by the name of kelp. A ton of good Irish kelp furnishes about 8lb. of iodine.

(488) *Sulphate of Soda*, ( $\text{NaO}, \text{SO}_3 + 10 \text{ aq}$ ); *Eq.* 71 + 90; *Sp. Gr. anhydrous*, 2.597, *crystallized*, 1.469.—This salt has long been known under the name of Glauber's salt. It crystallizes usually in long, four-sided prisms, terminated by dihedral summits. It is remarkably efflorescent, and loses the whole of its 10 equivalents of water by mere exposure, at common temperature, to the atmosphere. It has a saline, bitter taste, and is occasionally used medicinally as a purgative.

The solubility of sulphate of soda in water offers some remarkable anomalies. Water, at  $32^{\circ}$ , takes up 5.02 per cent.

(about one-twentieth of its weight) of the anhydrous salt; the quantity dissolved rapidly increases as the temperature rises; at  $60^{\circ}$  it dissolves 16 per cent., and at  $91^{\circ}$  F. water takes up about half its weight (50.65 per cent.) of the anhydrous salt; (the crystals contain more than half their weight of water, and consequently fuse on the application of a heat of  $100^{\circ}$ ). Beyond  $91^{\circ}$  F. the solubility of the salt decreases, so that a solution saturated at  $91^{\circ}$ , by simply elevating its temperature to the boiling point, is caused to deposit about one-sixth of the salt previously dissolved, in the form of acute rhombic octohedrons, which are anhydrous. The solution at its boiling point retains 42.65 per cent. of the salt. It has already been mentioned (70) that a boiling, saturated solution of this salt, if closed hermetically, may be kept for months without crystallizing, but the moment air is admitted, the whole becomes semi-solid from the sudden formation of crystals through the mass. Occasionally a few rhombic prisms, which, according to Löwel, contain eight equivalents of water, form in the mass. These crystals are more soluble than the hydrate with ten atoms of water. It is most probable, as Mr. Graham observes, that the salt exists in the super-saturated solution in the form of the eight-atom hydrate, and crystallization occurs when any circumstance occasions the formation of the more usual and less soluble ten-atom hydrate.

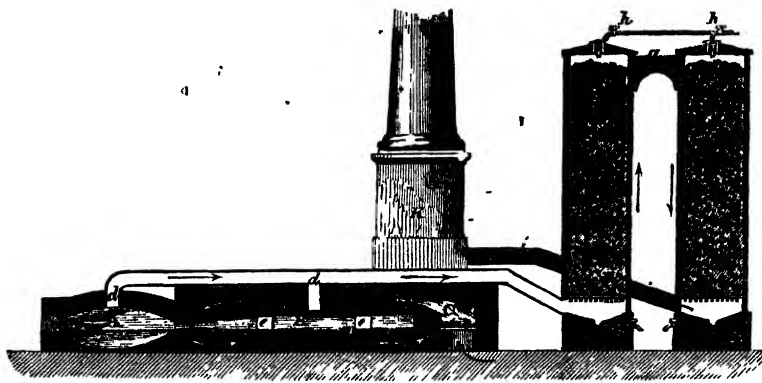
Sulphate of soda, to which the name of *Thénardite* has been given, has been met with nearly pure not far from Madrid, deposited at the bottom of some saline lakes, in anhydrous octohedra. It has also been found, not far from the same place, combined with sulphate of lime, as *Glauberite*, in anhydrous crystals.

*Preparation.*—Sulphate of soda is made from oil of vitriol and common salt in enormous quantities, under the name of *salt cake*, as a preliminary step in the manufacture of carbonate of soda. The operation is carried on in a reverberatory furnace, connected with an apparatus for condensing the hydrochloric acid, which, till within the last few years, was allowed to escape into the atmosphere to the serious injury of vegetation in the surrounding district. One of the best forms of furnace is shown in section in fig. 293: the course of the flues, however, is not exactly such as is there represented: A, the smaller of the two compartments which compose the furnace, is of cast-iron; into this (the *decomposer*) from five to six hundred weight of common salt are introduced, and an equal weight of sulphuric acid, of specific gravity 1.6, is gradually mixed with it; a gentle heat being applied to the outside, enormous volumes



of hydrochloric acid gas are disengaged, and pass off by the flue, *d*, to the condensing towers, *E* and *F*; these towers are filled with fragments of broken coke or stone, over which a continuous stream of

FIG. 292.



water is caused to trickle slowly from *h h*. A steady current of air is drawn through the furnace and condensing towers, by connecting the first tower with the second, as represented at *g*, and the second tower with the main chimney, *κ*, of the works. In the first bed of the furnace, about half the hydrochloric acid is expelled from the salt: the pasty mass thus produced is then pushed through a door for the purpose into the *roaster*, or second division, *B*, of the furnace. In this state it consists of a mixture of bisulphate of soda and undecomposed salt. The reaction in the first bed of the furnace may be represented as follows:



In the second stage of the operation a higher heat is required; the bisulphate of soda then reacts upon the unchanged chloride, and the conversion into neutral sulphate of soda is complete; thus  $\text{NaCl} + \text{HCl}, \text{NaO}, 2 \text{SO}_3 = \text{HCl} + 2 (\text{NaO}, \text{SO}_3)$ . The hydrochloric acid gas, as it is liberated from *B*, passes off through the flue, *d*, and is carried on to the condensing towers. Heat is applied to the outside of the roaster, *B*; the smoke and products of combustion circulating in separate flues around the chamber, in the direction indicated by the arrows, but never coming into contact with the salt cake in *B*.

A *double sulphate of potash and soda*,  $\text{NaO}, \text{SO}_3 + 3 (\text{KO}, \text{SO}_3)$  (Penny), may be formed by dissolving the two salts in water, and evaporating. Dr. Gladstone has shown that the employment of a

large excess of sulphate of soda does not alter the composition of the salt, the sulphate of soda in excess crystallizing in its usual form.

A *Bisulphate of Soda*, ( $\text{NaO}$ ,  $\text{HO}$ ,  $2 \text{SO}_3$ ; *Eq.* 120; *Sp. Gr.* 2.742), corresponding to bisulphate of potash, may be formed. It is more easily deprived of basic water by heat than the bisulphate of potash. The anhydrous salt, by a stronger heat loses its second equivalent of sulphuric acid, and may be employed as a convenient source of anhydrous sulphuric acid.

(489) *Sulphite of Soda*, ( $\text{NaO}$ ,  $\text{SO}_2$ ,  $+ 10 \text{ aq.}$ , *Eq.* 63 + 90), is now prepared largely under the name of *antichlore*, for the purpose of removing the last traces of chlorine from the bleached pulp obtained from rags in the manufacture of paper. It is procured by passing sulphurous acid obtained by the combustion of sulphur in air over moistened crystals of carbonate of soda, so long as the acid gas is absorbed; the mass is dissolved in water and crystallized. Sulphite of soda forms efflorescent prisms, which have a slight alkaline reaction and a sulphurous taste.

(490) *Nitrate of Soda*, ( $\text{NaO}$ ,  $\text{NO}_5$ , *Eq.* 85, *Sp. Gr.* 2.182), occurs abundantly on the surface of the soil, in the district of Atacama, in Peru, as nitre does in the East Indies. It is a somewhat deliquescent salt; it crystallizes in obtuse rhombohedra, and has a cooling, saline taste. When heated, it fuses at  $591^\circ \text{F.}$ , and at a higher temperature it undergoes decomposition. It is employed in the manufacture of nitric and sulphuric acids, but from its deliquescence cannot be substituted for nitrate of potash in gunpowder.

(491) *Carbonate of Soda*, ( $\text{NaO}$ ,  $\text{CO}_2$ ,  $10 \text{ aq.}$ ; *Eq.* 53 + 90; *Sp. Gr.*, *anhydrous*, 2.427, *hydrated*, 1.454. — The preparation of this salt constitutes one of the most important branches of chemical manufacture in this country, immense quantities of it being consumed in the production of glass, in the fabrication of soap, and in the preparation of the various compounds of soda.

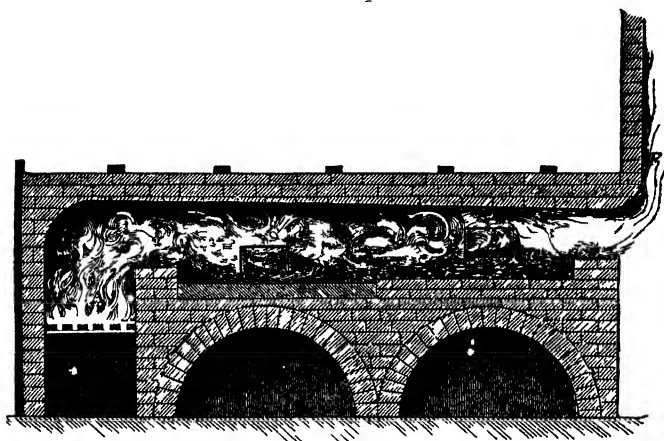
The greater portion of the carbonate of soda formerly employed was obtained from barilla, which is the ash furnished by burning marine plants. The salsola soda was extensively cultivated for this purpose on the southern coast of Spain, and on being burnt, yielded a semi-vitrified mass, which contained from twenty-five to thirty per cent. of carbonate of soda. The salicornia was cultivated for a similar purpose on the southern coast of France; but these sources of supply have almost entirely given way to a process by which the carbonate may be manufactured from sea-salt.

*Manufacture.*—In the process of manufacture a rough sulphate

of soda is first formed, in the manner already described (488). The sulphate of soda is then mingled with chalk and powdered coal in the proportion of 3 parts of sulphate of soda, 3 of chalk, and 2 of coal; and thrown, in quantities of about two hundred weight and a half at a time, into a hot reverberatory furnace, and frequently stirred, until the mass is thoroughly melted.

As the furnace, fig. 293, is constructed with two doors, D E,

FIG. 293.

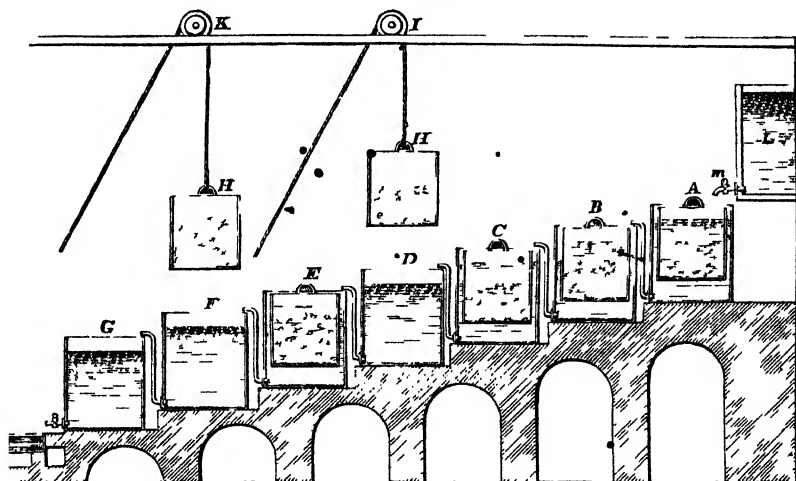


and a double floor, B C, one charge is introduced at the further door, E, whilst another, nearer the fire, is fusing at B; towards the conclusion of the operation the mass melts, and effervesces violently from the escape of carbonic oxide gas, which burns with a greenish or yellow flame; the mass is stirred briskly for a few minutes, and when completely and tranquilly fused, is raked out into a square trough or mould; when cold, this loaf is turned out, and forms *ball soda*, or *black ash*, containing about twenty per cent. of pure soda mixed with unburned coal and the oxysulphide of calcium. In order to extract the salts of soda from it, the black ash is broken up into coarse fragments, and digested with warm water for six hours, in vats provided with false bottoms: this washing is systematically carried on till the soluble portions are extracted, the last washings being employed to act upon fresh portions of ball soda.

One of the best forms of apparatus for the lixiviation of ball soda is shown in fig. 294. The principle on which it is constructed is simple, but it admits of extensive application; for in many cases much of the economy of a manufacturing process de-

depends upon the systematic washing of the product in such a manner as to extract the largest amount of soluble matter by means of the

FIG. 294



smallest quantity of water. In the case before us this is effected by placing the material for lixiviation, the black ash, in perforated sheet-iron vessels, *nn*, which can be raised or lowered into outer lixiviating vessels, also made of iron, by means of the cords and pulleys, *i*, *k*. When a charge is received from the furnace it is introduced into the lowest vessel, *G*, where it is submitted to the dissolving action of a liquid already highly charged with alkali from digestion upon the black ash contained in the tanks above it: after a certain time, this charge is raised by the rope from *G* into the tank *F*, where it is submitted to a weaker liquid, and so on, successively. The alkali at each stage becomes more completely exhausted, and the residue is successively submitted to the action of weaker ley, till at length, in *A*, it is acted upon by water only, supplied from the cistern, *L*. When fresh water is admitted from *m*, to the top of the vessel, *A*, as it is specifically lighter than the saline solution, it lies upon its surface, and gradually displaces the solution from *A*, through the bent tube, whilst the water takes its place, the liquid from *A* acts in a similar manner upon that contained in *B*; and this displacement proceeds simultaneously through each successive tier of the arrangement, until the concentrated ley flows off from *G*, and is transferred to the evaporating pans.

The insoluble residue contains almost the whole of the sulphur

originally present in the salt cake in the form of sulphide of calcium, together with the excess of lime and coal employed. It accumulates at the soda works till it forms a mountain of *soda waste*, to the annoyance both of the neighbourhood and of the manufacturer.

The water for lixiviation must not be employed at too high a temperature; if it be, it decomposes the oxysulphide of calcium. A black solution is thus obtained, which is allowed to settle, and is then pumped up into large, shallow, iron pans for evaporation. A large portion of the salt crystallizes during the ebullition, and is removed by means of perforated ladles. In order to convert the caustic soda which the solution contains into carbonate, it is evaporated to dryness, and after being mixed with sawdust is roasted in a reverberatory furnace: most of the sulphur escapes during this operation in the form of sulphurous acid; the residue yields the *soda ash*, or alkali of commerce, which contains about 50 per cent. of pure caustic alkali. If required in crystals, the crude carbonate thus obtained is redissolved, the liquid allowed to settle, and, while hot, is run into hemispherical pans, capable of containing 150 gallons of liquid, and about a ton of crystallized carbonate. The liquid cools in the course of five or six days; crystals of large size are formed; the mother-liquor is drained off by withdrawing a plug in the bottom, and it is then further evaporated down, and yields an ash of inferior quality.

The preparation of carbonate of soda, therefore, comprises three principal operations:

1st. The production of *salt cake*, or crude sulphate of soda, from common salt by the action of sulphuric acid.

2nd. The making of *black ash*, or impure carbonate of soda, mixed with sulphide of calcium, by deoxidation of the salt cake after mixture with chalk, by means of carbon.

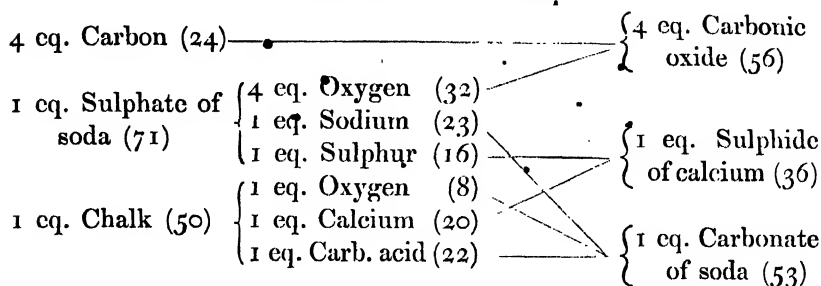
3rd. The preparation of *soda ash*, or the separation of the carbonate of soda from the black ash by lixiviating the latter in warm water and evaporating the solution to dryness.

Of these operations the most remarkable is the preparation of the black ash, by fusion of the sulphate with chalk and coal. The chemical changes which occur consist, first, in the deoxidation of the salt cake, and its conversion into sulphide of sodium with evolution of carbonic oxide; and secondly, in the formation of carbonate of soda and sulphide of calcium by interchange of the constituents of the sulphide of sodium and the carbonate of lime; the sulphide of calcium being rendered completely insoluble by the

excess of lime employed. These reactions occur simultaneously, and may be represented in the following scheme (omitting the excess of lime) :—

$\text{NaO}, \text{SO}_3 + 4 \text{C} + \text{CaO}, \text{CO}_2 = \text{NaO}, \text{CO}_2 + \text{CaS} + 4 \text{CO}$  ;  
or more distinctly, as follows :—

*Formation of Black Ash.*



An excess both of coal and of chalk are always employed in practice, as a good deal of coal burns off unavoidably, and an excess of lime renders the sulphide of calcium insoluble. Many attempts have been made to recover the sulphur from the soda waste, but hitherto without commercial success.

Various processes have, from time to time, been proposed to supersede the one just described, which was invented by Leblanc; and of late years works on a considerable scale have been established, in which, by roasting iron or copper pyrites directly with chloride of sodium, a sulphate of soda has been obtained without the preliminary manufacture of oil of vitriol. By the employment of poor ores of copper and tin it has been found possible to extract these metals with advantage from materials which would not otherwise have paid for working.

Mr. Tilghman takes advantage of the decomposition of chloride of sodium in the presence of alumina by steam at a high temperature, in order to obtain alkali from it. Precipitated alumina is made up into balls with chloride of sodium, and exposed to a current of steam in a reverberatory furnace strongly heated. Hydrochloric acid is expelled, soda is formed, and combines with the alumina;  $\text{Al}_2\text{O}_3 + \text{NaCl} + \text{HO} = \text{NaO}, \text{Al}_2\text{O}_3 + \text{HCl}$ ; when cold, the compound of alumina and soda is decomposed by a current of carbonic acid, and the carbonate of soda is dissolved from the alumina, which may be again employed for the same purpose.

*Properties.*—Carbonate of soda has a nauseous alkaline taste; it is an efflorescent salt, crystallizing in large, transparent,

rhomboidal prisms, which contain about 64 per cent. of water, and are soluble in any proportion in hot water, and even melt in their water of crystallization; they are also very soluble in cold water. The salt readily parts with its water, and melts at a red heat. Carbonate of soda, when crystallized between  $62^{\circ}$  and  $70^{\circ}$ , may be obtained in non-efflorescent crystals with eight equivalents of water: Mitscherlich has also obtained it with six equivalents of water. If crystallized above  $93^{\circ}$ , according to Berzelius, a salt is deposited which contains 5 equivalents of water, and crystallizes in forms derived from the square-based octohedron, whilst if crystallized between  $158^{\circ}$  and  $176^{\circ}$  four-sided prisms are produced, which contain only 1 equivalent of water.

(492) *Bicarbonate of Soda*, ( $\text{NaO}$ ,  $\text{HO}$ ,  $2 \text{ CO}_2$ ; *Eq.* 84; *Sp. Gr.* 2.192), is obtained by saturating a strong solution of the neutral carbonate with carbonic acid; the bicarbonate crystallizes in rectangular, four-sided prisms, which require 10 parts of water for solution at ordinary temperatures; and if the solution be heated, it loses one-half of the additional equivalent of carbonic acid, and is converted into sesquicarbonate.

A native *Sesquicarbonate of Soda*, ( $2 \text{ NaO}$ ,  $3 \text{ CO}_2$ ,  $4 \text{ HO}$ , *Eq.* 164), which, however, always contains sulphate of soda and chloride of sodium, has been long known in commerce as *trona* or *natron*; it is chiefly obtained as a saline efflorescence on the borders of some lakes, of which those of Egypt are the best known. Many other countries, however, such as those in the neighbourhood of the Black and Caspian Seas, as well as Thibet and Siberia, also furnish this salt. It crystallizes in rhombic prisms, terminated by four-sided pyramids; it is less soluble than the carbonate, but more so than the bicarbonate, and has a feeble alkaline reaction.

The carbonates of soda and potash, when melted together in the proportion of 1 equivalent of each, readily combine, and form a salt which fuses at a lower temperature than either of its components. On account of its ready fusibility this mixture is preferred to carbonate of potash or carbonate of soda alone, as a means of decomposing siliceous minerals in analytical operations (479). If carbonate of soda be dissolved in solution of carbonate of potash in excess, the solution, on evaporation, yields transparent crystals which, according to Margueritte, consist of  $2 (\text{NaO}, \text{CO}_2) + \text{KO}, \text{CO}_2 + 18 \text{ aq.}$  The salt is decomposed if it be attempted to recrystallize its aqueous solution, carbonate of soda being deposited.

(493) **PHOSPHATES OF SODA.**—Phosphoric acid forms with soda

several crystallizable salts: some account has already been given of these salts (370, 371, 372).'

*Neutral Tribasic Phosphate, or Subphosphate of Soda* ( $3 \text{ NaO}$ ,  $\text{PO}_5$ , 24 aq); *Eq.* 165 + 216; *Sp. Gr., cryst.*, 1.622. This salt is prepared from the rhombic phosphate by adding caustic soda to its solution till it feels soapy to the fingers. It crystallizes readily in small prisms, which effloresce in the air, and gradually absorb carbonic acid.

*Rhombic Phosphate of Soda*, ( $2 \text{ NaO}$ ,  $\text{HO}$ ,  $\text{PO}_5$  + 24 aq); *Eq.* 143 + 216; *Sp. Gr. crystallized*, 1.525.—This salt is the one from which most of the phosphates are formed; it is the one which has been longest known, and is that commonly called phosphate of soda. It is best procured by neutralizing with carbonate of soda the acid phosphate of lime, prepared as directed for obtaining phosphorus (365); carbonate of lime precipitates, and is allowed to subside, the clear liquid is then decanted from the precipitate, and set aside to crystallize. Phosphate of soda forms large, transparent, efflorescent rhombic prisms; they have a cooling saline taste, and are soluble in 4 parts of cold water, and very soluble in boiling water; the solution has a faint alkaline reaction. Dr. Clark found that when this solution is evaporated at temperatures above  $90^\circ \text{ F.}$ , the salt crystallizes with 14 equivalents of water; in both forms it is isomorphous with the corresponding arseniates of soda. If heated to  $300^\circ$ , it loses all its water of crystallization; but if redissolved in water, it may be obtained from its solution with all its characteristic properties. If a solution of this phosphate be mixed with free phosphoric acid, until it ceases to precipitate chloride of barium, another phosphate is produced, formerly known as the *biphosphate of soda* ( $2 \text{ HO}$ ,  $\text{NaO}$ ,  $\text{PO}_5$  + 2 aq, *Eq.* 121 + 18); it crystallizes with difficulty in right rhombic prisms, and has a strong acid reaction.

All these are tribasic phosphates, they precipitate nitrate of silver of a yellow colour.

*Pyrophosphate of Soda*, ( $2 \text{ NaO}$ ,  $\text{P}_2\text{O}_5$  + 10 aq); *Eq.* 134 + 90; *Sp. Gr., crystals*, 1.836.—If the rhombic phosphate be ignited it loses all its water, and on then treating it with water, a new salt dissolves, which crystallizes in prisms. It yields a dense white precipitate with nitrate of silver, which is not changed by exposure to light. Its solution has an alkaline reaction.

*Metaphosphate of Soda*, ( $\text{NaO}$ ,  $\text{PO}_5$ ); *Eq.* 103.—If the acid phosphate, or biphosphate, of soda be heated to redness, all its



water is expelled, the residue fuses to a clear glass, and on redissolving, the metaphosphate or monophosphate of soda is obtained. It forms a deliquescent and very soluble salt, which has a feeble but distinct acid reaction upon litmus. It cannot be obtained in crystals. The solution of this salt causes, with nitrate of silver, a white gelatinous precipitate; with nitrate of baryta or of lime a similar gelatinous precipitate is formed. This salt is susceptible of various modifications by the application of different temperatures (372).

(494) *Biborate of Soda*, ( $\text{NaO}, 2 \text{BO}_3 + 10 \text{aq}$ ; *Eq.* 101 + 90; *Sp. Gr.*, fused 2.367, crystallized 1.740), is well known in commerce under the name of *borax*. It is produced in considerable quantities in various parts of the world, particularly in Thibet, whence for many years the principal part of the borax consumed was supplied. The crude borax, or *tincal*, is obtained by the spontaneous evaporation of the waters of the lakes whence it is derived, and occurs crystallized in flattened six-sided prisms, terminated by trihedral summits. These crystals are, however, very impure, being covered with a greasy coating which requires removing; for this purpose the crystals are powdered, thrown upon a filter, and washed with a weak solution of caustic soda, which by forming a soap with the grease, dissolves and removes it; the remaining salt is dissolved in water. Carbonate of soda equal to one-eighth the weight of the borax is added to the solution, a copious precipitate ensues, the liquid is cleared by filtration, and allowed to cool very slowly: the borax is deposited in rectangular or in six-sided prisms, containing 10 equivalents of water.

A large quantity of borax is now manufactured from the boracic acid obtained from the lagoons of Tuscany, by saturating it with carbonate of soda, and allowing the salt to crystallize. In the course of this operation the crude boracic acid is mixed with about half its weight of soda ash, and is thrown in quantities of about three hundred weight at a time upon the floor of a reverberatory furnace; the mixture soon frits and effervesces, and must be well stirred during the process: a quantity of carbonic acid, of ammonia, and of organic matter which always accompanies the boracic acid, is got rid of in this operation. The fritted mass is then lixiviated in deep iron boilers. Here the solution is allowed to remain at rest in order to allow the impurities which consist chiefly of alumina, carbonate of lime, and some silica, to subside; and the liquid, when brought to a specific gravity of 1.166, is drawn off into wooden tanks, lined with lead, where the mass cools very slowly. The large

crystals in which borax is ordinarily sold, require much care to obtain them, they are procured only by operating on very large masses of the salt. Borax may also be obtained in octohedral crystals, which contain 5 equivalents of water, if the salt be allowed to crystallize from a solution of specific gravity 1.256, at a temperature between  $174^{\circ}$  and  $133^{\circ}$  F.

Borax has a feeble alkaline taste and reaction. The prismatic crystals are soluble in about half their weight of boiling water, and in 12 parts of cold water: they are slightly efflorescent. When heated, borax bubbles up, loses its water, and melts below redness into a transparent glass; this glass dissolves many metallic oxides which often impart intense and characteristic colours to the bead. Borax is hence much used as a test before the blowpipe for recognising the presence of certain metallic oxides. For this purpose a

small crystal of borax is fused upon the end of a bent platinum wire, as shown in fig. 295, and a minute quantity of the substance to be tested is melted with the salt in the flame of the blowpipe: the colour of the

FIG. 295.



glass varies according as the bead is heated in the oxidizing or in the reducing flame (404). The power which borax possesses of dissolving the metallic oxides renders it advantageous in the process of soldering oxidizable metals, to sprinkle the metallic surfaces with powdered borax; on the application of heat the borax melts as well as the solder, and the film of oxide which would otherwise prevent the adhesion is removed from the pieces of metal at the moment the alloy is presented to unite them. Borax is used in the arts as a flux, and by the refiner in the melting of gold and silver. In making enamels it is frequently added for the purpose of rendering the compound more fusible, and it is largely employed in fixing colours on porcelain.

Other borates of soda may be formed, but the biborate is the only salt of any practical importance; the quadriborate ( $\text{NaO}, 4 \text{BO}_3$ ) crystallizes with great difficulty: a neutral borate may be obtained by fusing 1 equivalent of ordinary borax with 1 equivalent of carbonate of soda; it crystallizes in oblique prisms ( $\text{NaO}, \text{BO}_3, 8 \text{aq}$ ).

(495) SILICATES OF SODA.—When finely divided silica is gradually added to fused carbonate of soda, carbonic acid is evolved with effervescence, and for each equivalent ( $\text{SiO}_2$ ) of silica added, one equi-

valent of carbonic acid is displaced, a neutral silicate of soda ( $\text{NaO}$ ,  $\text{SiO}_2$ ) being formed. A compound of similar composition is obtained, if carbonate of potash be substituted for carbonate of soda. Fritsche obtained a neutral silicate ( $\text{NaO}$ ,  $\text{SiO}_2$  9 aq) by dissolving in a strong solution of hydrate of soda a quantity of silica, equal in weight to the anhydrous soda present in the liquid: it crystallizes sometimes with 6, sometimes with 9 equivalents of water. When a concentrated solution of carbonate of soda is boiled with finely divided silica, a large proportion of the silica is dissolved, a gelatinous precipitate separates from the clear liquid as it cools, which, according to Forchhammer, consists of  $\text{NaO}$ , 36  $\text{SiO}_2$ . Other silicates have been obtained, to which the formulæ ( $2 \text{NaO}$ , 5  $\text{SiO}_2$ ), ( $\text{NaO}$ , 3  $\text{SiO}_2$ ) and ( $\text{NaO}$ , 4  $\text{SiO}_2$ ) have been assigned. It is difficult, however, to prove the existence of the three compounds last named. The neutral silicate has the property of dissolving in an excess of fused carbonate of soda, and the glass which is clear and transparent while hot, becomes opaque on cooling; but the same silicate, if heated sufficiently with an excess of silicic acid, melts, and forms a homogeneous mixture, which yields a transparent glass on cooling, the fusibility decreasing as the proportion of silica increases, until when the quantity of silica amounts to 9 equivalents, the heat of a forge is required for its fusion. These silicates are all more or less soluble in boiling water.

A peculiar silicate, which has received the name of *soluble glass*, is prepared by melting together 8 parts of carbonate of soda, or 10 of carbonate of potash, with 15 of pure quartz sand and 1 part of charcoal; the charcoal reduces the carbonic acid to carbonic oxide, and facilitates the decomposition of the alkaline carbonate: a black glass is thus obtained, which is not soluble in cold water, but is almost completely dissolved by 5 or 6 times its weight of boiling water. M. Fuchs, who first prepared this compound, has applied its solution to diminish the combustibility of wood and woven stuffs; a kind of fusible varnish, which is slightly hygroscopic, is formed over the surface of the material, and the access of atmospheric air to the fibre during combustion is impeded.

When heat is applied to the alkaline silicates, they do not at once become liquid, but pass through an intermediate viscous stage; they impart this viscosity, and the transparency which they preserve on cooling, to many other silicates if they are fused with them, and they destroy the tendency to crystallize on solidifying which the earthy and metallic silicates possess. This property is of the

highest importance to mankind, for upon it depend the most valuable properties of glass—ductility, which enables it to be moulded whilst in this intermediate state, and transparency, which renders it applicable to a multitude of important uses. The alkaline silicates are unable alone to resist the action of water and other solvents sufficiently to fit them for many of the applications of glass; but when combined with silicates of the earths, and certain metallic oxides, mixtures may be obtained after fusion which are no longer soluble in water or in acids.

### *Glass.*

(496) The composition of glass differs considerably with the nature of the purposes to which it is destined, but it consists mainly of mixtures, in varying proportions, of silicates of potash, soda, lime, baryta, magnesia, alumina, and lead, coloured by the addition of small quantities of different metallic oxides, particularly those of iron, manganese, cobalt, uranium, and gold.

The degree of fusibility of these different silicates varies considerably. The silicates of lime and of magnesia fuse when heated, *per se*, with great difficulty: the most fusible compound contains 2 equivalents of base to 3 of acid, the quantity of oxygen in the base being to that in the silicic acid as 1 is to 3. The silicates of protoxide of iron,  $2 \text{FeO}$ ,  $3 \text{SiO}_2$ , and of manganese, are readily fused, and crystallize on cooling. The silicate of lead,  $2 \text{PbO}$ ,  $3 \text{SiO}_2$ , is still more fusible, and on cooling forms a yellow, transparent glass. On the other hand, silicate of alumina,  $\text{Al}_2\text{O}_3$ ,  $2 \text{SiO}_2$ , is nearly infusible in the furnace.

All these silicates, however, when mixed with each other, or with the alkaline silicates, melt at considerably lower temperatures, the fusing point being generally much below that of the mean of the different silicates employed. The silicates of lime and alumina are nearly infusible when separate, but they melt readily after they have been mixed together.

Many of the properties of glass are familiar to all. It is a transparent, brittle solid, more or less fusible, and just before fusion possessed of remarkable ductility, a property which enables the workman to fashion it into the numberless forms which luxury or convenience dictate.

The different varieties of glass are not to be regarded as definite compounds, but as mixtures of various silicates in different proportions, with an excess of silica. It is generally found, however, in

the best kinds of glass that the mixtures are usually very nearly in such proportions that very little silica remains in the uncombined form. The proportion of silica to the bases is most conveniently expressed by ascertaining the proportion which the oxygen of the bases bears to that of the silicic acid. The subjoined table gives the result of some analyses of the more important kinds of glass:—

*Composition of Different Varieties of Glass in 100 parts.*

	Dumas.		Richardson.	Dumas.		Berthier.	Rowney.
	Bottle.	Window.		Plate.		Venetian.	Glass tube. Bohemian.
	French.	French.	English.	French.			
Silica . . . .	53.55	69.65	66.37	73.85	68.6		73.13
Potash . . . .	5.48			5.50	6.9		11.49
Soda . . . .		15.22	14.23	12.05	8.1		3.07
Lime . . . .	29.22	13.31	11.80	5.60	11.0		10.43
Magnesia . . .					2.1		0.26
Alumina . . . .	6.01	1.82	8.16	3.50	1.2		0.30
Oxide of iron .	5.74				0.2		0.13
Oxide of man- ganese. }					0.1		0.46
Ratio of the oxygen in the bases to that in the silica }	1 : 2	1 : 4	2 : 7	"	1 : 5		1 : 6

	Dumas.		Faraday.	Dumas.		
	Bohemian goblet.	Crown.		Guinand's optical.	Strass.	Enamel.
Silica . . . .	69.4	62.8	51.93	42.5	38.1	31.6
Potash . . . .	11.8	22.1	13.67	11.7	7.9	8.3
Lime . . . .	9.2	12.5		0.5		
Alumina . . . .	9.6	2.6		1.8	1.0	
Oxide of lead .			35.28	43.5	53.0	50.3
Oxide of tin .						9.8
Ratio of the oxygen in the bases to that in the silica }	1 : 4	1 : 5	1 : 6	1 : 4	2 : 7	3 : 7

(497) *Glass in which Silicates of Potash and Lime predominate.*

—The silicates of potash and lime are the principal components of the celebrated Bohemian glass, including the variety which is employed in the preparation of the hard glass of difficult fusibility, so much prized in the laboratory in the tubes used for the com-

bustion of organic compounds: the composition of this glass may be represented approximatively by the formula,  $\text{KO}, 3 \text{SiO}_2 + \text{CaO}, 3 \text{SiO}_2$ , part of the potash having its place supplied by soda, and part of the lime by magnesia, alumina, and traces of iron and manganese. The more fusible glass which is employed in the manufacture of the beautiful ornamental objects, for which Bohemia has long been distinguished, contains silicate of alumina, with silicates of potash and lime in a proportion which approaches  $\text{KO}, \text{SiO}_2 + 2 (\text{CaO}, \text{SiO}_2) + (\text{Al}_2\text{O}_3, 3 \text{SiO}_2)$ . The crown glass, employed for optical purposes, has nearly the formula  $\text{KO}, \text{SiO}_2 + \text{CaO}, \text{SiO}_2$ . (Dumas: *Ann. de Chimie*, II. xlv.) In the last two cases the proportion of oxygen in the bases to that in the silica is very nearly as 1 : 4.

In the finer kinds of glass potash is always employed in preference to soda, as the glass made from soda, however carefully the materials are selected, has a bluish-green tinge, which is not observed when potash is used.

(498) *Glass consisting of Silicates of Soda and Lime*.—French plate glass and ordinary window glass are the most important varieties of this description. Plate glass is very fusible, although the oxygen of the bases which it contains is only about one-sixth of that of the silicic acid. Soda produces a more liquid compound than potash. Care must be taken not to employ an excess of lime, as it is liable to render the glass milky on cooling, although it may be perfectly transparent whilst hot.

Great care is required in the selection of the materials employed in the manufacture of the finer kinds of glass. The ingredients used in the plate glass of St. Gobain are the following (Regnault):—

300	parts of white quartzose sand,
100	„ dry carbonate of soda,
43	„ lime, slaked by exposure to the air,
300	„ fragments of broken glass from previous meltings.

The fuel employed in the furnace is wood.

These materials are intimately mixed, and then melted in a large, deep, conical crucible, in which they are allowed to stand at a high temperature, for several hours, after they have been completely fused, in order that the impurities may subside. Quantities of this mixture sufficient for casting a single sheet are then removed, by means of copper ladles, into a smaller square crucible, termed the

*cuvette*.\* When the glass is thoroughly melted, the *cuvette* is removed from the furnace by a crane, and the glass is cast by pouring it upon a solid table of cast-iron; along the edge of this table are metal ledges, to regulate the thickness of the sheet of glass; the molten mass is immediately formed into a plate, and spread by means of a heavy, hollow, metallic roller. These sheets are next annealed by being placed in a heated oven, and allowed to cool very slowly down to the temperature of the air; an operation which requires from a week to a fortnight for its completion. They are then levelled by cementing one plate with plaster of Paris upon a slab, and causing a second plate to move, by machinery, over the surface of the first, the grinding material being fine sand and water; a level surface having been thus obtained, it is smoothed by emery of gradually increasing fineness, and the final polish is given by friction with finely levigated colcothar, or peroxide of iron.

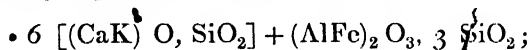
Window glass is made of a mixture of 100 parts of sand, with from 35 to 40 of chalk, 30 to 35 of soda ash, and from 50 to 150 of broken glass, or *cullet*. An equivalent amount of the cheaper sulphate of soda may be substituted in this mixture for the carbonate, as at a very elevated temperature the silicic expels the sulphuric acid; this decomposition may be facilitated by mixing the sulphate with about a tenth of its weight of charcoal; the sulphate is thus reduced to the form of sulphite of soda, which loses its acid at a lower temperature than the sulphate.

When carbonate of soda is used, the materials are first subjected to a heat insufficient completely to fuse the mass, and are *fritted* together, or heated until they agglomerate; moisture is thus completely expelled, and a part of the carbonic acid is got rid of; the frothing up of the mixture in the subsequent fusion, due to the expulsion of the carbonic acid, is also diminished, and the loss of alkali by volatilization is considerably lessened. The fritted mass is then transferred to other pots, and the temperature of the furnace is raised until complete fusion is effected. The mixture, after it has been thoroughly melted, is allowed to stand, in order that the bubbles of air may escape, and that the mass may become uniform in composition: the excess of sulphate of soda or of chloride of sodium which may have escaped decomposition rises to the surface and is skimmed off, forming what the manufacturer terms *glass-gall* or *sandiver*. The glass is then allowed to cool

\* In the Thames Plate-glass Works, the glass is melted in the same pot as that from which it is poured in casting. The pots are cylindrical, and not square, and the fuel employed is coal.

until it assumes the pasty, tenacious condition required for the manipulations of the glass-blower.

(499) *Silicates of Alumina, Lime, Iron, Magnesia, and Soda or Potash*.—The inferior descriptions of glass which are used for making wine bottles, carboys, and other articles in which a dark colour is unimportant, consist of a mixture of these silicates. The materials employed are of a coarser kind than those used in the preceding varieties of glass. A ferruginous or ochry sand, mixed with soapmaker's waste, are common ingredients. Mr. Pellatt gives the following as a composition employed in making bottle glass:—Sand, 100 measures; soaper's waste, 80; gas lime, 80; common clay, 5; and rock salt, 3 measures. The ordinary English bottles are of an olive-green colour, produced by the presence of protoxide of iron; while some of the German bottles are of a pale brown, resulting from a mixture of the oxides of iron and manganese. Bottle glass contains a smaller proportion of silica than any of the preceding varieties. One specimen, analysed by Dumas, presented a composition which would be approximatively represented by the formula,



whilst in a second specimen the composition would be more nearly represented by  $6 [(CaK) O, SiO_2] + 2 (AlFe)_2 O_3, 3 SiO_2$ . The oxygen of the bases, in the first instance, being in the proportion to that of the silicic acid as 1 to 2, and in the second case nearly as 2 to 3.

(500) Bottle glass is particularly liable to become devitrified by slow cooling, and to be converted into what is termed *Réaumur's porcelain*. In order to produce this effect, the glass may be imbedded in sand, or, still better, in a mixture of gypsum and sand, and heated up to a point sufficient to soften it, but just short of that required for its fusion. If it be now allowed to cool very slowly, it will be found to have entirely altered its aspect and properties; having become opaque and milk-white, and much resembling porcelain in appearance. It is now somewhat less fusible and less liable to crack on the application of sudden changes of temperature, and is much harder than the glass from which it was procured. It is a bad conductor of heat, but conducts electricity to a considerable extent, being comparable in this respect to marble (Pelouze). This alteration appears to be due to the partial separation of certain silicates, particularly of the silicates of lime and alumina, and their assumption of a more or



less definite crystalline form. This crystallization is sometimes very beautifully and perfectly exhibited in the residues at the bottom of the glass pots, which are allowed to cool down with great slowness and regularity. Nodules of opaque radiated crystals are there often found surrounded by a transparent glass. A mass of these opaque crystals, analysed by Dumas, presented a composition which corresponded with the formula  $18[(\text{CaNa})\text{O}, 2\text{SiO}_2] + 2(\text{Al}_2\text{O}_3) \cdot 9\text{SiO}_2$ ; the transparent glass from which they separated contained 3.5 per cent. less of silica, 1.4 less alumina, and a proportionately larger quantity of soda.

The devitrification of glass has recently been made the subject of experiment by Pelouze (*Chem. Gaz.*, Aug. 1855). He finds that the same sheet of glass may be devitrified, and again rendered transparent by fusion, many times in succession. Glass of any description may be devitrified, but the finer kinds of potash glass exhibit this phenomenon with difficulty. Pelouze found that the throwing in of a small quantity of sand, or even of powdered glass, into a pot which had cooled down to the viscid condition, greatly promoted the devitrification of the mass. The soluble soda glass of Fuchs, which contains 4 equivalents of silica to 1 of base ( $\text{NaO}, 4\text{SiO}_2$ ) is especially liable to devitrification from crystallization.

(501) *Silicates of Potash and Lead.*—The ordinary white glass in use in this country, commonly known as flint glass (the *cristal* of French writers), consists almost entirely of these silicates. The oxide of lead imparts a greater degree of fusibility and density, as well as a high refractive and dispersive power, in consequence of which such glass, from its superior brilliancy, is better fitted for the manufacture of ornamental articles, and from its greater softness is more easily cut and polished. Lead glass has, however, the inconvenience of being readily scratched, and it is liable to tarnish and change colour, especially if the proportion of alkali be large. According to Dr. Faraday's experiments, English flint glass contains one-third of its weight of oxide of lead; it may be represented very nearly by the formula,  $\text{KO}, 3\text{SiO}_2 + \text{PbO}, 3\text{SiO}_2$ . In a specimen from Newcastle, examined by Berthier, the proportion of silicate of lead was larger. This glass corresponded nearly to  $2(\text{KO}, 3\text{SiO}_2) + 3(\text{PbO}, 3\text{SiO}_2)$ . The composition of flint glass, however, is liable to considerable variation, even in different parts of the same pot, the lower portions having generally a greater density than those in the upper part of the pot. This arises from the density of the oxide of lead being much greater than that of

the other materials, so that it is extremely difficult to preserve a uniform mixture. Dr. Faraday found, for example, that glass taken from the top of pots not more than six inches deep, might have a density of 3.28, while that from the bottom might have a density of 3.85; in one instance, the glass at the top had a density of 3.81, that at the bottom of 4.75; and though these are extreme differences, there is no doubt that similar variations occur in every pot of glass made in the usual way. This variation in the density of the glass occasions great inconvenience in its application to the construction of optical instruments, owing to the difference of its refracting power in different portions of the same mass; and many endeavours have been made to overcome these defects. A lead glass of still higher refracting power was made by M. Guinand, in which the proportion of lead was very large, the formula being very nearly  $2 \text{ KO}, 2 \text{ SiO}_2 + 3 (\text{PbO}, 2 \text{ SiO}_2)$ , the proportion of oxygen in the bases being to that in the silica as 1 to 4: its specific gravity was 3.61. Dr. Faraday (*Phil. Trans.*, 1830, p. 10) proposed, for a similar purpose, a compound of silicate and borate of lead, the density of which is 5.44: this glass has a pale lemon-yellow tint, and consists of  $3 (\text{PbO}, \text{SiO}_2) + 3 \text{ PbO}, \text{BO}_3$ . Of late years a borosilicate of zinc has been introduced by MM. Macz and Clemandot into the glass used for optical purposes, with considerable success.

Much of the success in the preparation of glass for optical purposes depends upon the selection of pure materials, and also on their complete incorporation. The plan which succeeds best in attaining the latter object was introduced by M. Guinand. After the fusion is complete, the melted glass is thoroughly stirred with a paddle of crucible clay; the crucible and its contents are then allowed slowly to cool down in the furnace; when cold, the pot is broken, and the mass of glass cut *horizontally* into slices, by which means pieces of uniform density may generally be obtained. A good optical glass may be made from a mixture of 100 parts of pure sand, 100 of minium, and 30 of refined pearlash.

The oxide of lead which is employed in the manufacture of flint glass is not ordinary litharge (758), but minium or red lead (759), which is a higher oxide of lead, and is prepared with care from pure lead. The proportions of the materials usually employed in the manufacture of flint glass are, 300 of fine white sand, such as that from Lynn, on the coast of Norfolk, or from Alum Bay in the Isle of Wight, 200 of minium, and 100 of refined pearlash, with about 30 parts of nitre. In all cases the selection of mate-

rials for the melting-pot is of high importance. These pots are best made of an infusible clay, such as that of Stourbridge, which contains but little alumina and iron: 5 parts of clay and 1 of ground burnt pots are trodden into a mass by the workman, and allowed to stand for three or four months: the mixture is then carefully wrought into pots about four inches thick; great care being taken to exclude air-bubbles. The pots are allowed to dry for several months in a warm room, after which they are removed to an annealing oven, where they are raised very gradually to the temperature of the furnace. Flint glass is always made in pots which are arched over at top, and have an opening at the upper part of one side for the introduction of the charge and the withdrawal of the glass: they are set in the furnace in such a manner as to prevent the access of smoke and combustible gases to the interior, which would endanger the reduction of the oxide of lead to the metallic state. Plate glass, crown glass, and the other varieties of glass are made in open crucibles. The alumina, which is contained even in the finest glass, is chiefly derived from the action of the vitrified materials upon the clay of the pots.

(502) *Coloured Glasses.*—For the purpose of producing imitations of precious gems, a lead glass of still higher refracting power, termed *paste*, or *strass*, is employed, the proportion of oxide of lead exceeding 53 per cent.; the composition of this substance is very nearly represented by the formula  $(KO, 2 SiO_2 + 3 PbO, 2 SiO_2)$ ; the proportion of oxygen in the bases being one-fourth of that present in the silicic acid. A little borax is often added to this glass to increase its fusibility.

Glass of this description, when properly cut, is employed to imitate the diamond. The yellow colour of topaz is given to the strass by the addition of about 1 per cent. of peroxide of iron, or by a mixture of 4 per cent. of oxide of antimony with a minute proportion (0.1 per cent.) of purple of Cassius. The brilliant blue of sapphire is imitated by means of a small quantity of oxide of cobalt.

It is, indeed, a property of glass to dissolve small quantities of many of the metallic oxides without losing its transparency; but the glass becomes coloured with more or less intensity, and with different hues, according to the nature of the metallic oxide employed. Protoxide of iron, even in small quantities, communicates colours which vary from a pale green to a deep bottle-green, according to the proportion in which it is present: sesquioxide of iron, on the contrary, has but feeble colouring power, unless pre-

sent in considerable quantity, when it produces a yellow colour : protoxide of manganese is nearly colourless, but the sesquioxide communicates a violet tint to the glass. Advantage is taken of the knowledge of these facts in preparing colourless glass : protoxide of iron, in minute quantity, is a frequent impurity in the materials used, and it produces the green tinge often observed in ordinary glass : a minute quantity of black oxide of manganese corrects this, it imparts oxygen to the protoxide of iron, which thus becomes converted into the colourless peroxide, whilst the manganese itself being reduced to the state of protoxide exerts no injurious colouring effect. A little nitre or arsenious acid is sometimes added to glass instead of oxide of manganese, with a similar effect in converting the protoxide of iron into sesquioxide. Oxide of chrome imparts an emerald green tinge to glass ; oxide of cobalt a deep blue. A mixture of the oxides of cobalt and manganese gives a black glass ; black oxide of copper ( $\text{CuO}$ ) produces a green ; suboxide of copper ( $\text{Cu}_2\text{O}$ ) an intense ruby red ; whilst the sparkling appearance of aventurine is due to the dissemination of tetrahedral crystals of reduced metallic copper through the mass. Oxide of uranium communicates to the glass a peculiar opalescent yellow ; different shades of yellow are also produced by oxides of silver and of antimony, and by finely divided charcoal ; and a compound of gold with oxide of tin gives a magnificent ruby glass.

Sometimes glass is *flashed* or superficially coated with the coloured portion. A mass of colourless glass is in this case taken by the workman upon the end of his blowing tube, and then dipped into a pot of the coloured glass ; on blowing out the lump of glass, a vessel is obtained, the exterior layer of which is coloured, whilst the inner layer consists of colourless glass.

Painting on glass is effected by means of a very fusible glass, which when melted gives the required tint ; this glass is reduced to a very fine powder, and worked up with turpentine into a pigment : it is then applied with a pencil to the surface of a sheet of ordinary glass. The painted glass is afterwards subjected to a heat which is sufficient to melt the coloured glass, but is not intense enough to soften the glass to which it is applied.

*Enamel* is the term given to an opaque glass, which owes its opacity to the presence of binoxide of tin : a metallic ash is prepared by calcining at a low red heat a mixture of 1 part of tin with from 1 to 6 parts of lead, in a flat cast iron vessel ; the ash so obtained is mixed with sand and alkali, the proportions of which may vary considerably. In one recipe for the preparation of

enamel given by Knapp (*Chemical Technology*, translated by Ronalds and Richardson, vol. i. p. 137) the ashes of 4 parts of tin and 10 of lead are directed to be ground up with 10 parts of powdered quartz and 2 of pure soda ash. Other opaque bodies may be substituted for the oxide of tin in the preparation of enamel: in this manner bone ash, oxide of antimony, and even arsenious acid are sometimes employed to produce the opacity required. The enamel may be tinged of any colour by the suitable addition of metallic oxides. The enamel is applied with a brush to the surface to which it is to be attached, and is then fused by exposure to heat.

A modification of glass resembling enamel has been used to glaze cast iron pots, as a substitute for tinning. The pots having been first scoured with dilute sulphuric acid, and well rinsed in water, are brushed over with an enamel consisting of powdered flints ground with calcined borax, fine clay, and a little felspar; and while still moist, are dusted over with a glaze composed of felspar, carbonate of soda, borax, and a little oxide of tin. Having been thus prepared, the pots are next carefully dried, and finally the glaze is fused or *fired* under a muffle at a bright red heat. Oxide of lead, though it increases the fusibility of the glaze, should be carefully avoided, as it does not resist the action of acids in culinary operations.

(503) Well-made glass is unacted upon by any acid or mixture of acids except the hydrofluoric, which destroys it by combining with its silica. But it is not absolutely insoluble, though it is generally considered to be capable of withstanding the action of water. If glass be powdered and moistened with water, the liquid will dissolve a small quantity of alkali, sufficient to turn turmeric paper brown. If left long in water, or buried in moist earth, many kinds of glass become slowly disintegrated, and scale off in flakes which exhibit the brilliant colours of Newton's rings (110). This is particularly the case with the coarse glass used for wine bottles. Faraday found that some inferior kinds of bottle glass were rapidly destroyed by the action of dilute sulphuric acid.

At a high temperature water acts upon glass very rapidly; pieces of plate and window glass were suspended by Dr. Turner in the steam of a high pressure boiler, and in the course of four months specimens of plate glass one-fifth of an inch thick were completely decomposed; and Dr. Faraday found that flint-glass, under similar circumstances, was still more rapidly acted upon.

If glass be suddenly cooled after fusion, it becomes extremely brittle. When drops of melted glass are allowed to fall into water, they solidify in pear-shaped masses, which may be subjected

without breaking to considerable pressure, if gradually applied; but if the tail of one of these drops, known as *Rupert's drops*, be suddenly nipped off, the glass flies to pieces with a kind of explosion, and is shattered to powder. This effect appears to be due to the unequal tension to which the particles composing the drop are subjected, owing to the sudden cooling of the outer surface of the glass, while the interior is still dilated; as the mass cools, the particles within, by adhesion to the external solid portion, are still kept in their dilated state; but a very slight disturbance of their relative position suffices to overcome their equilibrium, and when once the mass gives way at any one point, the cohesion of the whole is destroyed.

Similar changes occur if glass articles are allowed to cool suddenly by exposing them whilst red hot to the external air. Glass objects of various descriptions, if their surface be but scratched, or if they be brought suddenly from a cold room into a warm one, will often crack and fall to pieces. In order to prevent this mislay, it is necessary to subject the different articles, after they have received their destined shape at the hands of the workman, to the operation of annealing, which is a very slow and gradual process of cooling, by which the parts are enabled to assume their natural position with regard to each other. Even then, since glass dilates considerably on the application of heat, and is likewise a bad conductor, a sudden and incautious elevation of temperature, such as that occasioned by pouring boiling water into a cold glass, often determines its fracture. Care is required during the process of annealing, especially with the coarser kinds of glass, not to raise the temperature too high; or otherwise devitrification to a greater or less extent would be liable to ensue.

(504) CHARACTERS OF THE SALTS OF SODA.—We have no good direct tests for the salts of this base, as it forms scarcely any even sparingly soluble compounds. Its most insoluble salt is what Fremy has termed the *bimetantimoniate* of soda (706), which is deposited in transparent octohedra when a solution of freshly prepared *bimetantimoniate of potash* is added to a neutral solution containing soda, provided that the liquid has been previously freed from all bases except the alkalies: 1 part of soda in 10,000 of water will produce a precipitate with this test after twenty-four hours. In analysis, a salt of soda is concluded to be present when the absence of every other base has been proved, and yet a saline residue remains, which with bichloride of platinum gives yellow striated prismatic crystals ( $\text{NaCl}$ ,  $\text{PtCl}_2$ ) by spontaneous evaporation. Dr. Andrey's (*Chem. Gaz.*, vol. x. p. 378) has pointed out

a property of this salt which admits of its identification in extremely minute quantities; a drop of the solution suspected to contain soda is mixed with a minute quantity of solution of bi-chloride of platinum, and allowed to evaporate in a warm place; if before it be quite dry it be placed in the field of the microscope, and examined by means of polarized light, minute crystals of the double chloride of sodium and platinum will be distinguished from the other salts by which they are accompanied, by their power of transmitting the polarized light, tinged with various colours, according to the thickness of the crystals. *Before the blowpipe* the salts of soda are known by the intense yellow which they communicate to the outer flame, if a fragment be introduced at the point of the blue cone upon a loop of platinum wire.

The salts of soda are in general more soluble than those of potash; the sulphates of the two alkalies afford a striking instance of this difference; the soda salts often effloresce when exposed to the air, whilst those of potash, on the other hand, frequently deliquesce, a fact well exemplified by the carbonates of the two bases.

### § III. LITHIUM.

*Symbol, L; Equivalent, 6.53; Specific Gravity, 0.5936.*

(505) LITHIUM, the metallic base of the third of the alkalies, is of comparatively recent discovery, and derives its name from λίθος (a stone), as it has been found only in the mineral kingdom: it is but rarely met with. The minerals of most frequent occurrence which contain lithia are the three under mentioned; they yield this alkali in proportions varying from 3 to 6 per cent. of their weight:—

Lepidolite, or lithia mica	2 [(LK) Fl] + 4 (Al <sub>2</sub> O <sub>3</sub> , 3 SiO <sub>2</sub> )
Triphane, or spodumene	3 [(LNa) O, SiO <sub>2</sub> ] + 4 (Al <sub>2</sub> O <sub>3</sub> , 3 SiO <sub>2</sub> )
Petalite	3 [(LNa) O, 2 SiO <sub>2</sub> ] + 4 (Al <sub>2</sub> O <sub>3</sub> , 6 SiO <sub>2</sub> ).

Metallic lithium, according to Bunsen (*Liebig, Ann.* xciv. 107) is easily reduced from its chloride by means of an electric current obtained from four or six pairs of the nitric acid battery. The metal is of a white colour, fusible at 356°, and is not volatilized by a red heat. It is harder than potassium, but softer than lead, and admits of being welded by pressure at ordinary temperatures; it can be drawn into wire, which, however, is inferior in tenacity to lead wire of the same dimensions. Lithium appears to be the lightest solid body known; it floats in naphtha, and has a density

of only 0.5936. A fragment of lithium burns upon a plate of mica with a very brilliant light, and a heat sufficiently intense to melt a hole in it: when thrown upon water it swims and becomes oxidized, like sodium. If thrown into nitric acid it usually takes fire.

(506) *Lithia* ( $\text{LO}$ , *Eq.* 14.5), the only known oxide of the metal, was discovered by Arfwedson, in 1818. It is extracted by carefully levigating the minerals that contain it, and igniting the fine powder with twice its weight of quick-lime. The mass is treated with hydrochloric acid, then with sulphuric acid, and the sulphate of lithia is dissolved out from the sulphate of lime; the last traces of lime are removed from the solution of sulphate of lithia by oxalate of ammonia. This solution may then be deprived of sulphuric acid, and converted into caustic lithia by the addition of baryta water; the solution on evaporation yields hydrate of lithia. This hydrate fuses readily below redness, and powerfully corrodes platinum vessels: silver capsules should therefore always be used in preparing it. This action upon platinum is one of the best indications of the presence of lithia.

*Chloride of Lithium* ( $\text{LCl} + 4 \text{ aq}$ ; *Eq.* 42 + 36) is one of the most deliquescent salts known; it is very soluble in alcohol, and crystallizes in cubes.

*Sulphate of Lithia* ( $\text{LO}$ ,  $\text{SO}_3 + \text{aq}$ , *Eq.* 54.5 + 9), crystallizes in flat tables, which are very soluble in water. The existence of bisulphate of lithia is doubtful.

*Soda Phosphate of Lithia* is one of the most characteristic salts of this alkali; it is insoluble in water containing alkaline phosphates. In order to prepare it, the insoluble metallic oxides and the earths, if present, are first precipitated, by adding carbonate of soda to the solution, evaporating it to dryness, and treating the residue with boiling water: phosphate of soda is then added, and the whole evaporated to dryness; the residue is treated with cold water, which removes the excess of phosphate of soda, and leaves the double phosphate of lithia and soda. This salt fuses with carbonate of soda to a glass which is transparent while hot, but becomes opaque on cooling. The proportion of lithia which it contains varies in different specimens.

*Carbonate of Lithia* ( $\text{LO}$ ,  $\text{CO}_2$ , *Eq.* 36.5), is only sparingly soluble in water, but is rather more soluble in solution of carbonic acid; it has an alkaline reaction upon turmeric. At a dull red heat it melts into a white enamel.

*Characters of the Salts of Lithium.*—Generally speaking the



salts of lithium are remarkably fusible: they are distinguished by yielding a white precipitate of carbonate of lithia in cold concentrated solutions with *carbonate of potash*, but the precipitate disappears on adding water and applying heat. On the addition of *phosphate of soda* the double phosphate of lithia and soda already mentioned is formed. *Before the blowpipe* they communicate a purplish red colour to the flame, and rapidly corrode platinum foil when heated on it.

#### § IV. AMMONIUM. (*Hypothetical.*)

*Symbol, H<sub>4</sub>N; Equivalent, 18.*

(507) When dry gaseous ammonia, H<sub>3</sub>N, is presented to the anhydrous oxyacids, such as sulphuric acid, SO<sub>3</sub>, sulphurous acid, SO<sub>2</sub>, or carbonic acid, the gas enters into combination with the acid, and a peculiar compound is formed, which does not constitute one of the ordinary salts of ammonia, and which differs in many important particulars from the compound which would be obtained by neutralizing a solution of the same acid in water with ammonia. In the latter case one of the ordinary 'salts of ammonia,' as they are usually termed, is produced; in the former case one of a series of compounds is formed for which no specific name has been proposed, but which may be conveniently distinguished as *ammonides*.\*

The general properties of these bodies may be illustrated by examining the several combinations formed between anhydrous sulphuric and sulphurous acids and dry ammoniacal gas.

(508) *Sulphuric Ammonide, Sulphatammon, (H<sub>3</sub>N, SO<sub>3</sub>); Eq. 57.*—When a current of dry ammoniacal gas is transmitted over anhydrous sulphuric acid, placed in a flask, and maintained at a low temperature, taking care to leave the acid somewhat in excess, a hard gummy mass is produced, which when exposed to the air, absorbs moisture and gradually deliquesces. The liquid

\* These compounds of ammonia with the anhydrous acids are often incorrectly spoken of as *amides*. Amides are, properly speaking, salts of ammonium which have been deprived of 2 equivalents of water. Of these compounds, oxamide, obtained by M. Dumas by the dry distillation of ammonia, was the first discovered, and it may be taken as the type of the class. Oxalate of ammonia may be represented by the formula (H<sub>4</sub>NO, C<sub>2</sub>O<sub>3</sub>); when this is distilled in a glass retort, it undergoes decomposition, and amongst other products a small quantity of the white insoluble compound termed oxamide is produced (H<sub>2</sub>NC<sub>2</sub>O<sub>2</sub>), which contains 2 equivalents of water less than the oxalate of ammonia. The ammonides contain only one equivalent of water less than the ordinary salts of ammonia. Sulphate of ammonia for instance may be represented as (H<sub>4</sub>NO, SO<sub>3</sub>) while sulphuric ammonide is (H<sub>3</sub>N, SO<sub>3</sub>).

thus obtained is saturated with carbonate of baryta in order to remove the excess of acid, and is then evaporated; it yields large transparent crystals derived from an octohedron with a square base. This compound is the parasulphatammon of Rose, and consists, according to this chemist, of  $(\text{H}_3\text{N}, \text{SO}_3)$ . It is freely soluble in water, but insoluble in alcohol. Its solution has a bitter taste, and gives no precipitate with salts of baryta, and none with bichloride of platinum. By long boiling with water or with a solution of tartaric acid, it is slowly changed into ordinary sulphate of ammonia: but if heated with a free alkali, sulphate of ammonia is speedily produced, and ammonia is expelled.

If ammoniacal gas in excess be made to act upon anhydrous sulphuric acid, another compound, isomeric with the former, termed *sulphatammon* by Rose, is obtained. It does not crystallize, and is quickly transformed when in solution into sulphate of ammonia.

A third compound, which may be procured in beautiful transparent crystals, is prepared by transmitting the vapour of anhydrous sulphuric acid into ammoniacal gas in excess; the solid compound thus obtained is fused in a current of dry ammonia, and dissolved in water. The crystals obtained on evaporation, according to M. Jacquelin, consist of  $3(\text{H}_3\text{N}) + 4 \text{SO}_3$ . Although the solution of this compound has an acid reaction, it gives no precipitate with salts of baryta.

(509) *Sulphurous Ammonide*,  $(\text{H}_3\text{N}, \text{SO}_2)$ .—If dry sulphurous acid gas be mixed with an excess of perfectly dry ammoniacal gas, 2 volumes of sulphurous acid and 4 of ammonia combine and form a yellow, amorphous, volatile, deliquescent compound, which when dissolved in water undergoes gradual decomposition.

If the sulphurous acid be in excess, a different compound is formed  $(\text{H}_3\text{N}, 2 \text{SO}_2)$ , corresponding in composition to bisulphite of ammonia from which 2 equivalents of water have been abstracted;  $\text{H}_3\text{N}, 2 \text{SO}_2 + 2 \text{H}_2\text{O} = (\text{H}_4\text{NO}, \text{HO}, 2 \text{SO}_2)$ . It is a reddish-yellow, crystalline, volatile substance, freely soluble in water; when in solution it is speedily decomposed into sulphate and trithionate of ammonia;  $2(\text{H}_3\text{N}, 2 \text{SO}_2) + 2 \text{H}_2\text{O} = \text{H}_4\text{NO}, \text{SO}_3 + \text{H}_4\text{NO}, \text{S}_3\text{O}_6$ . No such decomposition occurs when the ordinary bisulphite of ammonia is dissolved in water.

Anhydrous phosphoric and carbonic acids also form ammonides, which are analogous to those which have just been described.

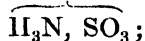
(510) Dry ammoniacal gas likewise unites with facility with the anhydrous hydric acids, but the compounds which are produced do

not correspond in properties to the ammonides, but, on the contrary, form ordinary salts of ammonia. For example, dry hydrochloric acid and dry ammoniacal gases unite with avidity, and a white solid compound is produced, which is ordinary sal ammoniac; when dissolved in water it gives with solution of nitrate of silver the usual curdy precipitate indicative of chlorine, and with bichloride of platinum the usual yellow double salt characteristic of ammonia is deposited.

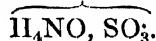
(511) *Theory of Ammonium.*—The differences between the characters of the compounds which dry ammonia forms with the anhydrous oxyacids, and those which it produces with the hydracids were very simply and beautifully explained by Berzelius with the aid of a hypothesis originally suggested by Ampère, which has been termed the ammonium theory, by the adoption of which the salts of ammonia admit of being considered as exhibiting a composition analogous to that which exists in the case of the metallic salts.

According to this view the compounds which are usually spoken of as salts of ammonia with the oxyacids, do not contain ammonia at all, but a compound in which the elements of an equivalent of water have been added to those of ammonia, ( $H_3N + HO$ ): in consequence of the assimilation of this equivalent of water, the substance which has united with the acid may be regarded as an oxide ( $H_4N, O$ ), like oxide of potassium or oxide of lead, but which contains the compound body, ammonium ( $H_4N$ ) in the place of a metal. Anhydrous ammonia when it unites with the anhydrous oxyacids, must therefore produce bodies very different from those obtained by the combination of hydrated ammonia with the same acids when hydrated, as may be seen, for instance, by comparing the formula of the compound with sulphuric acid in the two cases:—

Sulphuric ammonide.



Sulphate of ammonium.



It is likewise easy to see why by the combination of anhydrous ammonia with a hydracid equally free from water, a true salt of ammonium should be formed; for instance, hydrochloric acid and ammonia by their union yield chloride of ammonium, a salt which obviously presents the closest analogy with the metallic chlorides;  $H_3N + HCl = H_4N, Cl$ .

With the oxyacids, then, ammonia forms two classes of compounds; the more important class constitutes the normal salts

of the alkali in which the elements of water are necessarily present; the other class consists of the ammonides already described.

The theory of ammonium is supposed to derive considerable support from the following remarkable experiment:—If an amalgam of potassium or of sodium be moistened with a concentrated solution of sal ammoniac ( $\text{H}_4\text{NCl}$ ), the amalgam immediately begins to increase in bulk, and ultimately swells up till it acquires eight or ten times its original volume, and it at the same time assumes a pasty consistence, but still preserves its metallic lustre. This substance, if exposed to a temperature of  $0^\circ \text{F.}$ , crystallizes in cubes. It begins to decompose spontaneously immediately after its production, and the same effect occurs still more rapidly if it be placed in water; hydrogen gas is given off in minute bubbles, and ammonia is found in the solution. It is generally supposed that this remarkable amalgam consists of a combination of  $\text{H}_4\text{N}$  (or ammonium) with mercury. On attempting to expel the mercury by heat, however, the compound is decomposed, metallic mercury sublimes, and a mixture of hydrogen and ammoniacal gas is evolved: all other attempts to isolate the ammonium have been equally unsuccessful. The proportion of ammonium present in the amalgam, notwithstanding the great change experienced by the mercury, is extremely minute, amounting, according to Gay Lussac and Thénard, to little more than  $\frac{1}{20000}$ th of the weight of the mercury.

(512) The preparation of ammoniacal gas and of its aqueous solution have been already described (311). The solution in water has an intensely alkaline reaction, and may be regarded as a solution of oxide of ammonium,  $\text{H}_4\text{NO}$ ; but when heated, pure ammoniacal gas,  $\text{H}_3\text{N}$ , alone is expelled, and by passing the gas through a tube filled with quicklime to absorb the water which it carries over with it in suspension, ammonia may be obtained in a state of purity. The solution in water, when neutralized by acids and evaporated, yields salts of oxide of ammonium.

(513) SULPHIDES OF AMMONIUM.—Ammonium forms several sulphides which are freely soluble in water. The *protosulphide*,  $\text{H}_4\text{NS}$ , cannot be procured in a solid form; it may be prepared, like the protosulphide of potassium, by dividing a quantity of solution of ammonia into two equal portions, through one of which sulphuretted hydrogen is transmitted as long as it is absorbed; the saturated liquid is then added to the second portion of the solution. The protosulphide of ammonium dissolves many of the sulphides of the metals which form acids with oxygen (442). Many of these

double sulphides, such, for example, as those with the pentasulphides of antimony and of arsenic, and the tersulphide of molybdenum, may be obtained in crystals.

A *Bisulphide of Ammonium* ( $\text{H}_4\text{NS}_2$ ) may be obtained in large yellow, transparent, very deliquescent crystals, by passing sulphur and dry ammonia through a red-hot porcelain tube. In the hydrated form it has been long known as *Boyle's fuming liquor*, and is prepared by calcining 3 parts of slaked lime with 2 of sulphur, and distilling 3 parts of the mixture with 2 of sal ammoniac and 1 of sulphur; a yellow, oily, foetid liquor passes over, which fumes in the air, and on cooling deposits deliquescent, yellow, lamellar crystals; acids disengage hydrosulphuric acid and cause a deposit of sulphur. It dissolves a large quantity of sulphur, forming a *pentasulphide*,  $\text{H}_4\text{NS}_5$ , which crystallizes from its solution in long orange-yellow <sup>oblique</sup> ~~opaque~~ rhombic prisms.

*Hydrosulphate of Sulphide of Ammonium* ( $\text{H}_4\text{NS}, \text{HS}$ , *Eq. 51*), is the liquid commonly used as a reagent under the name of hydrosulphate of ammonia: it is formed by transmitting sulphuretted hydrogen through solution of ammonia to saturation. This liquid absorbs oxygen rapidly from the air, and the solution, which when newly-formed is colourless, becomes yellow from formation of bisulphide of ammonium, whilst a hyposulphite of ammonia remains in solution;  $2 (\text{H}_4\text{NS}, \text{HS}) + \text{O}_5 = \text{H}_4\text{NS}_2 + \text{H}_4\text{NO}, \text{S}_2\text{O}_3 + 2 \text{HO}$ .

The solution of this substance dissolves the sulphides of the electro-negative metals as readily as the protosulphide of ammonium does, but sulphuretted hydrogen is liberated from the hydrosulphate. Hydrosulphate of ammonia,  $\text{H}_4\text{NS}, \text{HS}$ , may be obtained in an anhydrous form by mixing dry sulphuretted hydrogen with dry ammoniacal gas, 4 volumes of ammonia combine with 2 volumes of sulphuretted hydrogen, and condense in yellowish, transparent, brilliant plates, which are very volatile, and sublime without decomposition; they are very soluble in water.

(514) *Chloride of Ammonium*, ( $\text{H}_4\text{N}, \text{Cl}$ ); *Eq. 535*; *Sp. Gr. 1.578*.—*Muriate of Ammonia*, or *Sal Ammoniac*, as it is commonly termed, is the most important of the salts of ammonium. It may be formed directly by the union of hydrochloric acid and ammoniacal gases; it was formerly imported from Egypt in considerable quantity as a product of the distillation of dried camel's dung, but in this country it is now furnished almost entirely from *ammoniacal liquor*, a waste product from the coal-gas works. Coal contains a portion of nitrogen, which, during the process of distilla-

tion, is partially converted into ammonia; this combines with carbonic acid and with sulphuretted hydrogen: these compounds condense with the gas liquor from which the ammonia is subsequently extracted. The best process for preparing sal ammoniac consists in neutralizing the gas liquor with hydrochloric acid. For this purpose the liquid is pumped up from the tank into the decomposer, a large wooden vat closely fitted with a cover, connected with flues for carrying off the gaseous products; the acid in suitable quantity is placed in jars, from which it is slowly drawn off by syphons, and is thus allowed gradually to mix with the liquor; abundance of gas is disengaged, and is made to pass through a fire where the hydrosulphuric acid is burned: much of the tarry matter derived from the coal, which was held in solution, is deposited during this operation, and the liquid froths up considerably, any loss which might be thus occasioned being prevented by the use of a waste pipe, by which the overflow is carried back into the well below. When the liquor has thus been neutralized, it is run into a covered evaporating pan, and the remaining portions of sulphuretted hydrogen are here expelled; after further concentration it is drawn off into shallow wooden vessels, lined with lead, to crystallize; the crystals which form are drained, and the mother liquor is again concentrated. The rough crystals are next heated in a cast iron pan, to a point approaching that at which sublimation commences; a good deal of tarry matter, which the salt still retains, is expelled during this roasting. The salt is then sublimed in a strong cylindrical iron pot, furnished with a leaden or iron cover lined with fire-clay; the fire underneath is gradually raised, and the salt sublimes and is deposited in large dome-shaped cakes on the inner surface of the cover.

The liquors which condense during the distillation of bones in closed iron cylinders, in the process of preparing animal charcoal, are highly charged with an impure carbonate of ammonia, contaminated with volatile, oily, and tarry matters derived from the action of heat upon animal matter: these liquors furnish a source of ammoniacal salts of some importance: formerly this liquid, after being subjected to a partial purification, was commonly known as spirit of harts-horn, because a similar liquor was originally obtained by the distillation of horn shavings.

Sublimed muriate of ammonia forms semi-transparent, tough, fibrous masses. It is very soluble in water, 100 parts of which at 60° dissolve 36 of the salt, and at the boiling point, 88.9 of the chloride are dissolved: a great reduction of temperature occurs

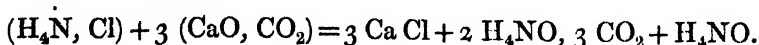
whilst it is dissolving, and it is hence employed as a common ingredient in frigorific mixtures; it crystallizes usually in an arborescent form, sometimes in cubes or octohedrons. Muriate of ammonia has a sharp acrid taste; it is slightly soluble in alcohol. When heated, it sublimes much below redness before undergoing fusion. It has a strong tendency to form double salts with the chlorides more electro-negative than itself.

(515) *Sulphate of Ammonia* ( $\text{H}_4\text{NO}$ ,  $\text{SO}_3$ ,  $\text{HO}$ , *Eq.* 66 + 9, *Sp. Gr.* 1.750) is prepared in large quantity by neutralizing gas liquor with sulphuric acid, but may be obtained pure by adding sesquicarbonate of ammonia to the acid so long as any effervescence ensues. It crystallizes in flattened prisms, which are isomorphous with those of sulphate of potash; it is soluble in twice its weight of cold water, and has a sharp disagreeable taste; when heated it decrepitates, melts, and sublimes unchanged. It forms a great number of double salts isomorphous with the corresponding salts of potash. An acid sulphate may be formed which has the formula ( $3 \text{H}_4\text{NO}$ ,  $\text{HO}$ ,  $4 \text{SO}_3$ ), and a double sulphate of soda and ammonia ( $\text{H}_4\text{NO}$ ,  $\text{NaO}$ ,  $2 \text{SO}_3 + 4 \text{aq}$ ) may be readily formed by mixing the two salts, and evaporating till crystals begin to form.

(515 bis) *Nitrate of Ammonia*, ( $\text{H}_4\text{NO}$ ,  $\text{NO}_5$ ); *Eq.* 80; *Sp. Gr.* 1.635.—This is a salt of some importance to the chemist, as it furnishes him with a ready source of pure protoxide of nitrogen. It is procured by saturating nitric acid with solution of sesquicarbonate of ammonia: on evaporation the salt crystallizes in long striated anhydrous prisms; by rapid evaporation it is obtained either in a fibrous or in an amorphous mass. It is readily soluble in cold water, is somewhat deliquescent, and has a bitter acrid taste; when heated to  $392^\circ$  it melts, and at  $480^\circ$  it undergoes complete decomposition, being converted into protoxide of nitrogen and water, in the manner already described (305);  $\text{H}_4\text{NO}$ ,  $\text{NO}_5 = 2 \text{NO} + 4 \text{HO}$ . If thrown on a red hot plate it melts, hisses, and is dispersed with a faint bluish-flame.

(516) *Compounds of Ammonia with Carbonic Acid*.—There are several carbonates of ammonia. The most important of these is the *sesquicarbonate* ( $2 \text{H}_4\text{NO}$ ,  $3 \text{CO}_2$ , *Eq.* 118), the common carbonate of the shops. It is usually obtained as a semi-transparent fibrous mass by mixing chalk with half its weight of muriate of ammonia, and subliming the mixture at a temperature below that of boiling water; the salt is received in leaden hoods, in the interior of which it is deposited. During this process a large quantity of free ammonia escapes, as the neutral carbonate

of ammonia cannot exist at that temperature. The decomposition may be represented thus :—



The sesquicarbonate of ammonia has a strong pungent smell, like that of pure ammonia, arising from the continual volatilization of the neutral carbonate at ordinary temperatures. It has an acrid taste and a strong alkaline reaction. Its aqueous solution, if saturated and exposed to a temperature of 32° F., deposits large transparent octohedra with a rhombic base. According to the rescachies of Rose there are several compounds resulting from the combination of carbonate of ammonia with different proportions of bicarbonate of ammonia.

The *Bicarbonate of Ammonia* ( $HO, H_4NO, 2 CO_2$ , *Eq.* 79, *Sp. Gr.* 1.586) is isomorphous with the corresponding potash salt; it is soluble in 8 parts of cold water, and if the solution be heated carbonic acid escapes; when exposed to the air the dry salt slowly volatilizes. It may be obtained in large transparent prismatic crystals, derived from a rhombic octohedron,  $2 (HO, H_4NO, 2 CO_2) + HO$ , by pouring boiling water upon the sesquicarbonate, corking the flask, and allowing it to cool. It is sometimes formed spontaneously during the decomposition of guano, and is then deposited in large regularly formed crystals.

Carbonate of ammonia combines with many metallic carbonates, forming double salts.

(517) *Phosphates of Ammonia*, corresponding to those of soda, may be formed; but the only one of any importance is the tribasic phosphate of soda, oxide of ammonium, and water, known as *microcosmic salt* ( $HIO, NaO, NH_4O + PO_5 + 8 aq$ ); *eq.* 138 + 72.

is prepared by mixing a hot solution of 6 parts of phosphate of soda with a solution of 1 part of muriate of ammonia in the smallest possible quantity of water; common salt remains in solution, and the phosphate crystallizes in large transparent prisms, which are efflorescent in a dry air. It may be purified by a second crystallization from a small quantity of hot water, to which a little free ammonia has been added to compensate for the loss of ammonia which the salt sustains when heated in solution. By ignition all the oxide of ammonium and water are expelled, metaphosphate of soda remains, and fuses into a colourless glass at a red heat. This salt is sometimes employed as a flux for experiments with the blowpipe, as the glass dissolves many metallic oxides and forms transparent beads, from the colour of



which the presence of certain metals, in many cases, can be ascertained.

(518) *Ammoniated Salts*.—Anhydrous ammonia enters into combination with many anhydrous metallic salts, in a manner somewhat analogous to that of water of crystallization. In other cases, salts which usually retain water of crystallization lose it either partially or entirely when they combine with ammonia, but the number of equivalents of ammonia is not influenced by the proportion of water with which the salt generally unites. Chlorides of silver, tin, copper, and calcium, sulphate of copper and of zinc, nitrate of silver and of copper, are instances of this kind of combination. The composition of some of these salts is exhibited in the subjoined table:—

		Eq.	Sp. Gr.
Ammoniated chloride of silver . .	$\text{AgCl} + 2 \text{H}_3\text{N}$ . . . .	177.5	
1 Ammoniated chloride of copper . .	$\text{CuCl} + 3 \text{H}_3\text{N}$ . . . .	118	
2 Ammoniated chloride of copper . .	$\text{CuCl} + 2 \text{H}_3\text{N}, \text{HO}$ . . . .	110.5	1.671
3 Ammoniated chloride of copper . .	$\text{CuCl} + \text{H}_3\text{N}$ . . . .	84	2.194
Ammoniated chloride of tin . . . .	$\text{SnCl} + \text{H}_3\text{N}$ . . . .	110	
Ammoniated chloride of calcium . .	$\text{CaCl} + 4 \text{H}_3\text{N}$ . . . .	123.5	
Ammoniated sulphate of silver . . .	$\text{AgO}, \text{SO}_3 + 2 \text{H}_3\text{N}$ . . . .	190	2.218
Ammoniated sulphate of copper . . .	$\text{CuO}, \text{SO}_3 + 2 \text{H}_3\text{N}, \text{HO}$ . . . .	122.5	1.790
Ammoniated nitrate of silver . . . .	$\text{AgO}, \text{NO}_5 + 2 \text{H}_3\text{N}$ . . . .	200	
Ammoniated nitrate of copper . . . .	$\text{CuO}, \text{NO}_5 + 2 \text{H}_3\text{N}$ . . . .	127.5	1.874

These compounds when exposed to the air lose a portion of the ammonia; if heat be applied, the ammonia is often entirely expelled, as in the case of ammoniated chloride of silver, the compound originally employed by Faraday for obtaining ammoniacal gas in the liquid form (182). The chloride of silver is left unaltered when the ammonia is expelled. In other instances the elements of ammonia react upon the salt and decompose it. Ammoniated chloride of copper,  $\text{CuCl}, 3 \text{H}_3\text{N}$ , when heated, undergoes the following decomposition;  $(\text{CuCl}, 3 \text{H}_3\text{N}) = \text{Cu}_2\text{Cl} + \text{H}_4\text{NCl} + \text{H}_3\text{N}$ . The corresponding compound of nickel is reduced to the metallic state.

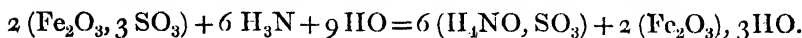
In solution ammonia also combines with many metallic salts, forming analogous compounds: by exposure to air the ammonia escapes. Salts of zinc form a colourless solution with excess of ammonia; those of cobalt give a pink, which passes into green; whilst the salts of nickel and of copper give a violet blue solution.

(519) *Action of Ammonia upon Salts in Solution*.—From what has been already stated it is evident that ammonia acts upon metallic salts not merely as a powerful base as in cases where potash or soda are made to act upon them. The results produced

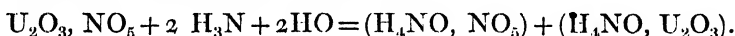
by the addition of ammonia to a solution of a metallic salt may be stated as follows :—

1. If the ammonia be insufficient in quantity to neutralize the whole of the acid contained in the metallic salt, a sparingly soluble subsalt of the metal may be precipitated: in this way subsulphate of copper, subnitrate of lead, or subsulphate of alumina may be formed; for instance,  $4 (\text{CuO}, \text{SO}_3) + 3 \text{H}_3\text{N} + 7 \text{HO} = 3 (\text{H}_4\text{NO}, \text{SO}_3) + (4 \text{CuO}, \text{SO}_3, 4 \text{aq})$ .

2. If the ammonia be present in excess, it may combine directly with the acid of the salt, and produce with it a soluble salt of ammonia, whilst a precipitate of the metallic oxide in a hydrated form is occasioned; as when oxide of chromium, peroxide of iron, or alumina is thrown down from its salts:—for example,



3. Sometimes the ammonia if in excess combines with the precipitated oxide, as it does with peroxide of uranium, when mixed with solution of permanganate of uranium:—



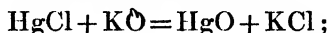
4. In other cases a double salt of ammonia and the base may be precipitated, as when phosphate of ammonia is mixed with a salt of magnesia, in which case a double phosphate of magnesia and ammonia is formed and deposited in crystals:  $2 (\text{MgO}, \text{SO}_3) + 3 \text{H}_4\text{NO}, \text{PO}_5 = 2 (\text{H}_4\text{NO}, \text{SO}_3) + (\text{H}_4\text{NO}, 2 \text{MgO}, \text{PO}_5)$ .

These four modes of action may however occur, and indeed frequently do occur, when a fixed alkali, such as potash or soda, is mixed with a metallic salt.

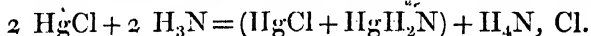
5. A soluble compound may be formed, into the composition of which both the metallic oxide and the ammonia enter, and unite with the acid so as to form a species of double subsalt. Hydrate of magnesia, hydrated oxide of copper, of zinc, of cobalt, or of nickel, when free from acid, are very sparingly dissolved by a solution of pure caustic ammonia, but a mixture of chloride of ammonium, or even of carbonate of ammonia, with caustic ammonia, dissolves them without difficulty. The compounds thus formed are similar in nature to those produced when the dry salts of the metals absorb ammoniacal gas, and form compounds which have a definite composition, as is shown in the table just given. The solutions of these salts in ammonia frequently absorb oxygen rapidly if exposed to the air: salts of iron, manganese, and cobalt furnish examples of this kind.

6. But it occasionally happens that the ammonia enters into

the composition of the salt in a more intimate manner. When a solution of corrosive sublimate ( $\text{HgCl}$ ) is mixed with solution of potash, a yellow precipitate of oxide of mercury is formed, and chloride of potassium remains in solution :—



but the case is otherwise if ammonia be added; a white precipitate is then formed, the composition of which is unchanged by the addition of an excess of ammonia. Sir R. Kane (*Phil. Mag.* June, 1836, p. 495) showed that this compound consists of  $\text{HgCl} + \text{HgH}_2\text{N}$ . Its formation may be explained by the following equation :



From this result, conjoined with others obtained from an examination of other ammoniacal derivatives from copper, palladium, and other metals, Kane was led to propose a new theory of the composition of ammonia. He argues that ammonia is not a direct compound of hydrogen with nitrogen, but rather a combination of an equivalent of amidogen with an equivalent of hydrogen; so that he represents ammonia as  $\text{HAd}$  ( $\text{Ad}$  standing for amidogen,  $\text{H}_2\text{N}$ ); the equivalent of hydrogen being liable to displacement by an equivalent either of mercury, or of certain other metals. One equivalent of such an amide of mercury ( $\text{HgAd}$ ) is, according to Kane, contained in white precipitate, in combination with 1 equivalent of chloride of mercury.

Later experiments, however, especially those of Hofmann, on the formation of bases by substitution from ammonia, have not strengthened the theory proposed by Kane; they have shown that not only 1 equivalent of hydrogen admits of being displaced by some equivalent substance, but that all 3 of the equivalents of hydrogen in ammonia admit of being thus displaced; nay more, that bodies may be obtained which are derived from ammonium, in which all the 4 equivalents of hydrogen in this compound have been displaced by other equivalent bodies. We shall recur to these experiments when considering the properties of the organic bases.

7. Within the last few years several remarkable bases have been formed which are derived from ammonia, but into the composition of which certain metals enter. Although these compounds contain the elements of ammonia, and of the oxides of the metals, yet they do not give any indications either of ammonia or of their component metals by means of the ordinary tests.

In this manner several series of compounds have been formed, some of which contain platinum, others contain cobalt, and others

palladium; in most instances they form crystallizable and well characterized salts.

Amongst the compounds thus formed 4 of those obtained from platinum may be selected by way of illustration. The first of these contains a base for which Gerhardt has proposed the name of *platosamine*,  $\text{PtH}_3\text{NO}$ ; the second, he has termed *diplatosamine*,  $\text{PtH}_6\text{N}_2\text{O}$ , + aq; the third, *platinamine*,  $\text{PtH}_3\text{NO}_2$  + 2 aq; and the fourth, *diplatinamine*,  $\text{PtH}_6\text{N}_2\text{O}_2$ . The base last mentioned has not as yet been obtained in a separate form.

With hydrochloric acid each of these bases forms a crystallizable salt, the composition of which is represented by the empirical formula given in the second column of the following table, whilst the third column shows the relation of the compound to the chloride of platinum from which it is obtained; the first two compounds being derived from the protochloride of platinum, the last two being formed from the bichloride of platinum:—

Chloride of platosamine . .	$\text{PtH}_3\text{N Cl}$ or $\text{PtCl, H}_3\text{N}$
Chloride of diplatosamine . .	$\text{PtH}_6\text{N}_2\text{Cl}$ or $\text{PtCl, 2H}_3\text{N}$
Chloride of platinamine . .	$\text{PtH}_3\text{N Cl}_2$ or $\text{PtCl}_2, \text{H}_3\text{N}$
Chloride of diplatinamine . .	$\text{PtH}_6\text{N}_2\text{Cl}_2$ or $\text{PtCl}_2, 2\text{H}_3\text{N}$ .

(520) CHARACTERS OF THE COMPOUNDS OF AMMONIUM.—The salts of ammonium are colourless; they are all decomposed by heat, unless the acid itself be capable of volatilization, in which case they generally sublime without change. They are distinguished from the salts of all the metals, with the exception of the alkaline bases, by the absence of any precipitate when their solutions are mixed with solution of carbonate of potash or of soda.

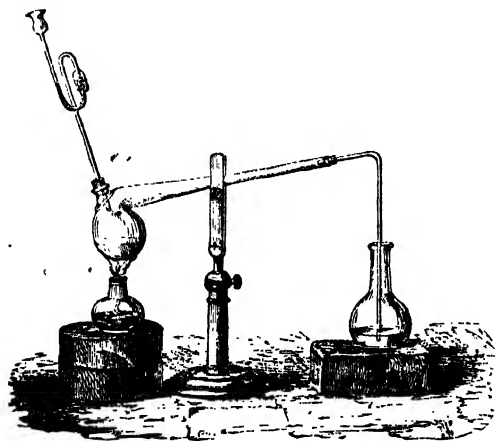
The salts of ammonium may be recognised by heating them in the solid form with *quick lime* or with *caustic potash*, when pungent fumes of ammonia are extricated: if their solutions be boiled with either potash or lime a similar extrication of ammonia ensues, and if the quantity of ammonia be too small to be detected by the smell, *a rod dipped in hydrochloric acid* produces white fumes when brought into the vapour; these fumes are due to the production of sal ammoniac, which is formed by the union of the gaseous ammonia with the vapour of the hydrochloric acid, and precipitates in the solid form.

*The Phosphomolybdate of Soda* is also an extremely delicate test for the presence of a salt of ammonium in solution. The mode of preparing and applying it is described under the head of molybdic acid (692).

(521) *Estimation of Ammonia.*—The most accurate method of determining the quantity of ammonia in any substance, if the absence of potash has been ascertained, consists in precipitation by the *bichloride of platinum*, observing all the precautions mentioned when speaking of its use with potash; a yellow insoluble double salt falls, consisting of  $\text{PtCl}_2 + \text{H}_4\text{NCl}$ : it contains, in 100 parts, 7.65 of ammonia. This salt is easily distinguished from the corresponding compound of potassium by heating it to redness: metallic platinum alone remains; whereas the potassium salt though decomposed by this treatment, leaves chloride of potassium, which may be dissolved out of the residue.

(522) The following method of determining the amount of ammonia in guano or in crude ammoniacal salts will often be found

FIG. 296.



useful. One hundred grains of the matter for trial is placed in a small retort, fig. 296, and two ounces of water are added: by means of a bent funnel half an ounce of solution of potash, of specific gravity 1.25, is also introduced; about an ounce and a half of liquid is gradually distilled into the flask, which contains a measure of 1000 water grains of sulphuric

acid (one burette full, fig. 290) diluted to the strength required for the determination of soda for alkalimetric purposes (480). As soon as about an ounce and a half of liquid has been distilled, the contents of the retort are allowed to cool a little, and another ounce of water is introduced into the retort by the funnel; a second distillation is then proceeded with, until the quantity of water just added has passed over; an ounce more of water is added to the contents of the retort, and the distillation is renewed until this additional quantity of water has passed over: the liquid in the flask is then decanted into an evaporating basin; the flask twice rinsed out with a small quantity of distilled water, and the washings are added to the acid liquid. This is now to be neu-

tralized in the usual way, by means of a standard solution of soda, this soda solution being of such a strength that one measure of it exactly neutralizes an equal measure of the acid liquid originally introduced into the flask. Suppose that this liquid from the flask now requires 67 measures of soda solution instead of 100; 33 measures of the acid will have been neutralized by the ammonia; a quantity of ammonia will therefore have passed over equivalent to 33 grains of soda. The corresponding quantity of ammonia may be calculated from the equivalent numbers of the two alkalies:—

$$\begin{array}{ccc} \text{Eq. NaO.} & \text{Eq. H}_3\text{N} & \\ \text{Thus, } 31 & : 17 & :: 33 : 18\cdot09. \end{array}$$

100 grains of the material operated on in this case would therefore have contained 18·09 grains, or 18·09 per cent. of ammonia.

## CHAPTER XII.

### GROUP II.—METALS OF THE ALKALINE EARTHS.

#### § I. BARIUM.

*Symbol, Ba; Equivalent, 68·64.*

(523) BARIUM occurs abundantly under the form of sulphate of baryta, and is not unfrequently found as carbonate of baryta. Davy first procured it in the metallic state by making mercury the platinode of a voltaic battery in a strong solution of hydrate of baryta; the barium was thus obtained as an amalgam, from which the mercury was expelled by strongly heating it in a green glass tube filled with hydrogen; but it does not appear to have been thus obtained in a state of purity. When procured by the voltaic decomposition of its fused anhydrous chloride, it is of a pale yellow colour; it is malleable, and is fusible at a red heat. Barium decomposes water rapidly at ordinary temperatures. In the air it is quickly tarnished by absorbing oxygen. It decomposes glass at a red heat.

(524) *Compounds of Barium with Oxygen.*—Baryta forms two oxides, a protoxide, BaO, and a peroxide, BaO<sub>2</sub>: the first is the only one which forms salts.

*Baryta, BaO; Eq. 76·6; Sp. Gr. 4.*—Anhydrous baryta may be obtained by exposing the nitrate to a red heat in a capacious porcelain crucible; the salt decrepitates, melts, and then boils up

and gives off a large quantity of oxygen, leaving the baryta as a grey porous mass, which absorbs moisture and carbonic acid if exposed to the air. Mixed with one-eighth of its weight of water it slakes, forming a hydrate with extrication of great heat. - Baryta may be fused before the oxyhydrogen blowpipe.

The sulphide of barium may be employed for procuring pure *hydrate of baryta*, by boiling its solution with oxide of copper: hyposulphite of baryta and disulphide of copper, which are both of them insoluble, are produced, and hydrate of baryta dissolves;  $6 \text{ BaS} + 8 \text{ CuO} = 5 \text{ BaO} + \text{BaO}_2 + \text{S}_2\text{O}_2 + 4 \text{ Cu}_2\text{S}$ ; the hot liquid is filtered, and crystals of the hydrate are deposited as the solution cools. They contain 10 equivalents of water, and are soluble in 3 times their weight of boiling water, and in 20 of cold water; the liquid has a strong alkaline reaction. When exposed to the air both the crystals and the solution absorb carbonic acid; by heat 9 equivalents of water are expelled from the crystals, and a monohydrate is left, which fuses at a heat above redness, and retains its water at all temperatures. Hydrate of baryta is sparingly soluble in alcohol.

*Peroxide of Barium* ( $\text{BaO}_2$ , *Eq.* 84.6) is formed by passing oxygen over anhydrous baryta at a low red heat; or by mixing pure baryta with an equal weight of chlorate of potash and heating to low redness; in the latter case ignition commences at one point, and spreads through the mass like tinder;  $6 \text{ BaO} + \text{KClO}_3 = \text{KCl} + 6 \text{ BaO}_2$ : the chloride of potassium may be dissolved out by water, and a bulky white hydrated peroxide of barium ( $\text{BaO}_2 + 6 \text{ aq}$ ), insoluble in water, remains. By strong ignition the peroxide of barium again parts with its oxygen. Boussingault has proposed to make use of caustic baryta as a means of preparing oxygen on a large scale by alternately passing atmospheric air over the baryta, raised to a dull red heat, and then expelling the absorbed oxygen by intense ignition: these processes may be repeated for an indefinite number of times upon the same portion of baryta, in an apparatus contrived for the purpose (*Ann. de Chimie*, III., xxxv.) The anhydrous peroxide combines with water when moistened, without evolving any sensible amount of heat, and crumbles down to a white powder: it is used for procuring the deutoxide of hydrogen.

(525) *Sulphides of Barium*.—Of these the most important is the protosulphide,  $\text{BaS}$ , *Eq.* 84.6. The preparation of this substance from the native sulphate of baryta presents some interest to the chemist, as it enables him to obtain with ease the soluble

salts of baryta from its insoluble sulphate. In order to prepare the sulphide, the native or artificial sulphate is reduced to a very fine powder and intimately mixed with an equal weight of starch or flour, or with one-tenth of its weight of powdered charcoal, made up into a paste with oil, and introduced into a crucible lined with charcoal: the cover is luted on, and the crucible and its contents are exposed for an hour to an intense heat. By this treatment the sulphate of baryta is deoxidized, carbonic oxide escaping, whilst sulphide of barium remains:  $\text{BaO}, \text{SO}_3 + 4 \text{C} = \text{BaS} + 4 \text{CO}$ . The mass, when treated with boiling water, dissolves, and the sulphide is deposited as the solution cools in colourless transparent crystals, with 6 equivalents of water: when treated with hydrochloric, or any other acid, the sulphide of barium is decomposed, and the corresponding salt of baryta is formed, whilst sulphuretted hydrogen escapes; thus  $\text{BaS} + \text{HCl} = \text{BaCl} + \text{H}_2\text{S}$ .

(526) *Chloride of Barium*, ( $\text{BaCl}$ , 2 aq); *Eq.* 104.1 + 18; *Sp. Gr. cryst.* 3.144.—This salt is obtained by dissolving the sulphide of barium or the carbonate of baryta in hydrochloric acid. It crystallizes in flat four-sided tables, containing 2 equivalents of water, which may be expelled by heat: water dissolves nearly half its weight at  $60^\circ$ , and three-fourths at  $212^\circ$ : this solution is the usual test for ascertaining the presence of sulphuric acid in solutions, which it indicates by the formation of a white precipitate insoluble in nitric acid. If anhydrous baryta be introduced into a jar of hydrochloric acid gas it becomes incandescent, chloride of barium is formed, and water condenses on the sides of the vessel.

The *Silicofluoride of Barium* ( $\text{BaF}$ ,  $\text{SiF}_2$ , *Eq.* 140) is procured by adding silicofluoric acid to a salt of baryta; it is quickly deposited in microscopic crystals, which are insoluble in an excess of the acid. This salt is anhydrous. It is decomposed by ignition, which converts it into fluoride of barium. The silicofluoride of strontium is soluble.

(527) *Sulphate of Baryta* ( $\text{BaO}, \text{SO}_3$ , *Eq.* 116.6, *Sp. Gr.* 4.59) is the principal native mineral of baryta. It occurs in volcanic rocks in large veins, and is found accompanying the ores of lead and other metals. It is met with both massive, and crystallized in modifications of the right rhombic prism. The name baryta is derived from the high specific gravity of this compound, which is about 4.5. It is insoluble in water, and in all the acids except boiling concentrated sulphuric acid: as the solution in this acid cools, crystals of the sulphate are deposited: at a bright red heat the sulphate fuses into a white enamel: and by boiling the powdered



sulphate of baryta with carbonate of potash or soda, the artificial sulphate is partially converted into the carbonate. It may be easily formed by precipitating a salt of baryta by any soluble sulphate, when it falls as a heavy white powder. Sulphate of baryta is used as a *permanent white* by artists in water colours. It is also employed for adulterating white lead; when ground with oil, however, it becomes partially transparent, and impairs the opacity of the lead pigment.

*The Nitrate of Baryta* ( $\text{BaO}$ ,  $\text{NO}_3$ , *Eq.* 130·6, *Sp. Gr.* 3·284) crystallizes in anhydrous octohedrons, when a solution of the carbonate of baryta in nitric acid is evaporated. It is insoluble in alcohol, and requires 8 or 10 times its weight of cold water, and 3 of boiling water, for solution. Nitric acid precipitates it in crystals from its solution, unless very dilute: when heated, it decrepitates strongly; on ignition, the whole of the acid is expelled, and pure baryta remains.

(528) *Carbonate of Baryta* ( $\text{BaO}$ ,  $\text{CO}_2$ , *Eq.* 98·6, *Sp. Gr.* 4·4) forms the mineral called *witherite*; it occurs, both massive and crystallized, usually in six-sided prisms terminated by six-sided pyramids. It is abundant in the lead veins in the north of England, and is also found in Styria and in Siberia. It is easily prepared artificially by precipitating a salt of baryta by an alkaline carbonate; it then forms a white powder, which is very sparingly soluble in pure water, and is insoluble in water charged with saline matter: an aqueous solution of carbonic acid dissolves it rather freely. Ignition of the carbonate does not expel the carbonic acid, but if it be mixed with charcoal and intensely ignited, it is partially decomposed, and pure baryta is formed, which may be dissolved out with water. If mixed with an equal weight of carbonate of lime, carbonate of baryta is decomposed without much difficulty when ignited in a current of steam. The hydrate of baryta may be dissolved out of the mixture by water.

Carbonate of baryta is now manufactured to some extent as a substitute for a portion of the alkali in the making of plate and flint glass. The silicate of baryta fuses and becomes incorporated with the other silicates. This carbonate is prepared from the sulphate, which is reduced to the form of sulphide by ignition with carbonaceous matter, and the sulphide is dissolved in water, and decomposed by a current of carbonic acid: the carbonate precipitates as a fine white powder (Richardson and Ronalds's translation of Knapp's *Technological Chemistry*, vol. ii. p. 450).

(529) **CHARACTERS OF THE SALTS OF BARYTA.**—The salts of

baryta are colourless. The carbonate and all the soluble salts act as powerful poisons, and have an acrid, disagreeable taste. The best antidote, when they have been taken internally, is the sulphate of soda or of magnesia.

Salts of baryta when in solution are easily recognised by giving with *sulphuric acid* a white precipitate of sulphate of baryta, which is insoluble in the acids. Baryta is, for the purposes of analysis usually estimated in the form of sulphate; 100 parts contain 65.63 of baryta, and 34.37 of sulphuric acid.

With *carbonate of potash* or of *soda* a white precipitate of carbonate of baryta is produced in solutions which contain baryta. *Hydrosulphate of ammonia* gives no precipitate in such solutions. Salts of baryta, when mingled with alcohol, tinge its flame of a yellow colour. They are distinguished from the salts of strontia by forming an insoluble silicofluoride of barium when mixed with *silicofluoric acid*, and by yielding no immediate precipitate with *oxalic acid*, which, however, on standing causes the separation of tufts of acicular crystals of oxalate of baryta.

## § II. STRONTIUM.

*Symbol*, Sr; *Equivalent*, 43.84; *Specific Gravity*, 2.54.

(530) STRONTIUM is an element much less abundantly diffused than barium, which it closely resembles in properties. It is found both as carbonate and as sulphate, and is procured in the metallic state in the same way as barium, to which it bears a relation similar to that existing between potassium and sodium. Strontium is a malleable metal of a pale yellow colour. When heated in the air, it burns with a yellowish flame, emitting sparks. Water is decomposed by it with evolution of hydrogen: dilute nitric acid dissolves it, but the concentrated acid is almost without action even when boiled upon it.

*Strontia* (SrO, Eq. 52) may be obtained from its nitrate by ignition. When mixed with water it slakes, and forms a hydrate which crystallizes with 10 equivalents of water. These crystals require 50 times their weight of cold and 2 of boiling water for solution; 9 equivalents of water are expelled by heat, the remaining equivalent being fixed at all temperatures; at a full red heat the latter hydrate fuses: both the hydrate and its solution rapidly absorb carbonic acid from the air.

The *Chloride of Strontium* (SrCl 6 aq, Eq. 79.5 + 54, Sp. Gr.

*cryst.* 2·015) crystallizes in slightly deliquescent needles, which require less than their weight of cold water for solution; alcohol dissolves it, and burns with a crimson flame. Chloride of strontium is rendered anhydrous by a moderate heat; if heated strongly it fuses.

*Silicofluoride of Strontium* ( $\text{SrF}$ ,  $\text{SiF}_2$ , *Eq.* 116) is prepared by adding silicofluoric acid to a salt of strontia; it is tolerably soluble in water, thus furnishing a character which distinguishes the compounds of strontia from those of baryta.

*Sulphate of Strontia* ( $\text{SrO}$ ,  $\text{SO}_3$ , *Eq.* 92, *Sp. Gr.* 3·9), the *celestine* of mineralogists, is found crystallized in prisms isomorphous with those of sulphate of baryta; it is, however, easily distinguished from it by its lower density. Sulphate of strontia is very sparingly soluble in water, but is taken up by boiling sulphuric acid. It may be formed by mixing a solution of any sulphate with a solution of a salt of strontia.

*Nitrate of Strontia* ( $\text{SrO}$ ,  $\text{NO}_3$ , *Eq.* 106, *Sp. Gr.* 2·704) crystallizes from hot concentrated solutions in anhydrous octohedrons, which are soluble in 5 parts of cold water and half their weight of boiling water; by crystallizing it at a low temperature it may be obtained in efflorescent crystals with 5 equivalents of water. If strongly heated, it decrepitates, and then loses acid and leaves pure strontia. It is used by the makers of fireworks to give a splendid crimson colour to their flames, and is prepared by them by reducing the native sulphate to sulphide by heating it with charcoal, dissolving the sulphide in water, and decomposing it with dilute nitric acid. It crystallizes best from an acid solution. A mixture of 40 parts of nitrate of strontia, 5 of chlorate of potash, 13 of sulphur, and 4 of sulphide of antimony deflagrates with a magnificent red colour; the mixture is dangerous both to prepare and to preserve, having more than once been the occasion of frightful accidents to the manufacturers from its becoming ignited spontaneously. Nitrate of strontia is insoluble in alcohol.

*Carbonate of Strontia* ( $\text{SrO}$ ,  $\text{CO}_2$ , *Eq.* 74, *Sp. Gr.* 3·65), the *strontianite* of mineralogists, occurs both massive and crystallized. Mere ignition is insufficient to expel carbonic acid from this salt. It is scarcely soluble in water, but is dissolved by a solution of carbonic acid. The process of preparing it consists in precipitating a salt of strontia by an alkaline carbonate.

(531) CHARACTERS OF THE SALTS OF STRONTIA.—The salts of strontia are all colourless: they have a bitter acid taste, but are not poisonous. They are distinguished *before the blowpipe* by the

red colour which they communicate to the flame. Reagents produce the same effects as upon salts of baryta, excepting that neither *silicofluoric acid* nor the *hyposulphite of soda* yields any precipitate in the solutions of the salts of strontia. *Oxalic acid* gives an immediate turbidity in them. The compounds of strontia are distinguished from those of lime by the gradual formation of a white precipitate on agitation after the addition of a solution of *sulphate of lime*. The sulphate of strontia is used for determining the amount of this earth in analysis: it contains in 100 parts 56.82 of strontia.

### § III. CALCIUM.

*Symbol*, Ca; *Equivalent*, 20; *Specific Gravity*, 1.578.

(532) CALCIUM forms one of the most abundant and important constituents of the crust of the globe. It is the metallic basis of lime. Calcium occurs in nature in combination with fluorine, forming the different varieties of fluorspar; it is still more abundant in the various forms of carbonate of lime, in which it is united with oxygen and carbonic acid; and it is also met with in large quantities as gypsum, which is a hydrated sulphate of lime.

Calcium was obtained by Dr. Matthiessen (*Q. Journ. Chem. Soc.* viii. 28) by the electrolytic decomposition of a mixture consisting of 2 equivalents of chloride of calcium and 1 equivalent of chloride of strontium. The mass may be fused in a Hessian crucible, in the centre of which is placed a porous tube filled with the same mixture, and into this an iron wire passed through the stem of a tobacco pipe is inserted: this wire is connected with the platinode of the battery, the anode of which consists of a plate of sheet iron bent into a cylindrical form, and immersed in the melted mass exterior to the porous tube: the calcium is reduced and preserved from oxidation by so regulating the heat that a film of solidified salt shall form upon the surface of the mixture in the porous cell.

Calcium is a light yellow metal, of the colour of gold alloyed with silver; in hardness it is intermediate between lead and gold; it is very malleable and can readily be hammered into leaves thinner than writing paper. It melts at a red heat. At ordinary temperatures it tarnishes within a day or two, even in dry air, and in the presence of moisture it is slowly oxidized. Heated to redness on platinum foil, it burns with a brilliant scintillating white light. It readily amalgamates with mercury: when heated in chlorine, or

in the vapour of bromine, iodine, or sulphur, the combustion is accompanied by an extremely vivid light. Water is rapidly decomposed by calcium, lime being formed and hydrogen evolved. Concentrated nitric acid does not attack the metal until heated to the boiling point, though it is rapidly dissolved by the dilute acid. Dr. Matthiessen found that the chloride of calcium is not decomposed by heating it with potassium or sodium; and he concludes that the properties formerly assigned to calcium were really due to a mixture of potassium with aluminum and silicon.

(533) *Linne*, (CaO); *Eq.* 28; *Sp. Gr.* 3.08 (Le Royer and Dumas).—Calcium forms only one oxide—viz., lime, which has been known from time immemorial. It is obtained in a state of purity by heating pure carbonate of lime to full redness; this carbonate occurs very nearly pure either in black or in Carrara marble, which if burnt in an open fire for an hour or two, yields it very nearly free from foreign matters. For commercial purposes, common limestone, which is an impure carbonate of lime, is burned in a kiln, the cavity of which is usually either egg-shaped, or in the form of an inverted truncated cone: it is charged with alternate layers of coal and limestone, and the fire is kindled. The lime, as it is burnt, gradually sinks down, and is removed by openings at the base of the furnace, and a fresh supply of coal and limestone is supplied at the top of the kiln. The limestone should not be too dry; that which has recently been quarried answers best. In damp weather, too, the operation succeeds better than in a dry state of the atmosphere; indeed, the process is facilitated by injecting steam into the kiln, although in practice the advantage which is gained does not compensate for the increased expense and trouble. Carbonate of lime cannot be decomposed without the concurrence of aqueous vapour; an interchange between the steam and the carbonic acid appears to be thus effected, but the hydrate which is produced is quickly destroyed again.

Pure lime, or quick lime, is a white caustic powder, which has hitherto resisted all attempts to fuse it.

*Hydrate of Lime* (CaO, HO), *Eq.* 37; *Slacked Lime*.—When water is poured upon lime, it swells up and enters into combination with the water; if the proportion of water be not too great, a light dry powder is formed, attended with a powerful extrication of heat: so great is the heat thus developed that fires have several times been traced to this source. The hydrate which is formed is a definite compound of 1 equivalent of water with 1 equivalent of lime. Lime, when exposed to the air, slowly attracts both water and

carbonic acid; as a result of this action it falls to powder, and becomes what is termed *air slacked*; in this case a compound is gradually formed, which consists of an equivalent of carbonate with an equivalent of hydrate of lime,  $\text{CaO}$ ,  $\text{CO}_2 + \text{CaO}$ ,  $\text{H}_2\text{O}$ .

Lime is soluble in about 700 parts of cold water; this solution is known as lime water; the earth, however, is less soluble in hot than in cold water, so that if lime water saturated in the cold be raised to the boiling point, half the lime is deposited, and is redissolved as the solution cools. Lime water is much employed as a test for the presence of carbonic acid, which instantly renders it turbid: it has a distinct alkaline reaction, and an acrid taste: by evaporating it in vacuo, Gay Lussac obtained from it the protohydrate of lime crystallized in hexahedral plates. Hydrate of lime is decomposed by a red heat, and pure lime remains.

*Milk of lime* is merely hydrate of lime diffused through water: in slacking lime for its preparation, and indeed, generally where the hydrate is required in a fine state of subdivision, it is best to use boiling water in quantity nearly equal to twice the weight of the lime; the powder may afterwards be readily diffused through cold water.

(534) *Mortars and Cements*.—The great consumption of lime in the arts is for the purpose of making mortars and cements. Pure lime, when made into a paste with water, forms a somewhat plastic mass, which sets into a solid as it dries, but it gradually cracks and falls to pieces. It does not possess sufficient cohesion to be used alone as a mortar; to remedy this defect and to prevent the shrinkage of the mass the addition of sand is found to be necessary. Ordinary mortar is prepared by mixing 1 part of lime into a thin paste with water, and adding 3 or 4 parts of sharp sand, of tolerable fineness: the materials are then thoroughly incorporated, and passed through a sieve to separate lumps of imperfectly burned lime: a suitable quantity of water is afterwards worked into it, and it is then applied in a thin layer to the surfaces of the stones and bricks which are to be united. The bricks or stones are moistened with water before applying the mortar, in order that they may not absorb the water from the mortar too rapidly. The completeness of the subsequent hardening of the mortar depends mainly upon the thorough intermixture of the lime and sand.

The theory of the hardening of mortar is obscure. The mortar gradually becomes dry upon its surface, and at the same time it absorbs carbonic acid from the air; but this change is never complete, for the central portions, after a lapse of many ages, are still

found to contain free lime in abundance: mortar taken by Dr. Malcolmson from the Great Pyramid was still found to contain a large proportion of hydrate of lime. A mixture of carbonate of lime with the lime appears to set harder than pure lime only. A gradual combination also takes place between the lime and the silica of the sand: each grain of sand thus becomes superficially converted into a hydrated silicate of lime, forming a compound which by degrees acquires considerable hardness, and contributes greatly to the solidification of the mortar. All old mortar, when treated with an acid, yields a small proportion of gelatinous silica.

Limestones vary greatly in composition; being rocks of sedimentary origin, they are not pure chemical substances, but consist of a mixture of various bodies, in which carbonate of lime is the prevailing ingredient. The different varieties of limestone are distinguished according to the nature of the most important of these admixtures. Thus a limestone is described as magnesian, argillaceous, ferruginous, sandy, or bituminous, according as it is characterized by the presence of carbonate of magnesia, clay, oxide of iron, sand, or bituminous matter. These different limestones, when burned, yield lime of very different characters, which are particularly manifested by the action of water upon them. The purer the lime, the more quickly does it combine with water when mixed with it. Such pure limes are technically termed *rich* or *fat* limes; they slack rapidly, during which operation they swell up and greatly increase in bulk; they become extremely hot, and yield a soft, fine, dense paste: while those which contain much magnesia, silica, or alumina, slack slowly, emit but little heat, and are technically termed *poor*.

In slacking for mortar, a fine smooth paste is required: in order to secure this point, the slacking should be effected quickly, with about 3 parts of water to 1 of lime; the mass then swells to between 3 and 4 times its former bulk; if too little water be used, a crystalline granular hydrate is formed.

The temperature required for burning lime varies with the composition of the limestone. When a siliceous limestone is burnt, the silica combines with the lime if the temperature be too high and be too suddenly raised, and a coating of silicate forms on the surface of the mass, which becomes partially vitrified. Such lime slacks very imperfectly, and is said to be *dead burnt*. Occasionally dead burnt lime is a basic carbonate,  $2 \text{ CaO}, \text{CO}_2$ , which is produced by insufficient burning (Fuchs).

(535) Ordinary mortar, when placed in water, gradually softens and disintegrates, whilst the lime dissolves away. It

cannot therefore be used for subaqueous constructions. Some poor limes, however, which contain from 10 to 30 per cent. of finely divided silica or clay, furnish a mortar which possesses the valuable property of hardening under water, forming what are termed *hydraulic limes*. These limes may be artificially imitated by mixing with the lime a due proportion of clay not too strongly burnt. At Puzzuoli, near Naples, a porous volcanic material is found which has received the name of *puzzuolana*. This substance, when powdered and mixed with ordinary lime, confers upon it the property of yielding an excellent hydraulic mortar. It is found that a puzzuolana which is easily attacked by sulphuric acid is more effective than one which resists the action of the acid. Puzzuolana consists chiefly of silicates of alumina, lime, and soda. Elsner gives the following as the composition of a sample of puzzuolana which he analysed:—

Matter soluble in acid 49'01	{	Silica . . . . .	11'50
		Oxide of iron . . . .	11'77
		Alumina . . . . .	17'70
		Lime . . . . .	3'16
		Magnesia . . . . .	2'15
		Potash . . . . .	0'29
Matter insoluble in acid 42'98	{	Soda . . . . .	2'44
		Silica . . . . .	37'43
		Oxide of iron . . . .	0'57
		Alumina . . . . .	1'25
		Lime . . . . .	2'25
		Magnesia . . . . .	0'27
Water . . . . .	{	Potash . . . . .	0'08
		Soda . . . . .	1'12
			<hr/> 7'65
			99'64

Many other substances, when added to lime, confer upon it hydraulic properties to a greater or less extent. Carbonate of magnesia is one of these. If ordinary quick lime be reburnt at a dull red heat, it also acquires hydraulic properties (Capt. H. Scott). M. Vicat (whose treatise on mortars and cements contains a mass of valuable information and careful investigation on this important practical subject) established a manufactory of hydraulic lime at Meudon, near Paris. Four parts of chalk were ground and levigated in water with 1 part of clay, so as to obtain a very intimate mixture of the materials, which were allowed to subside, moulded into blocks, dried, and calcined at a carefully regulated temperature. *Portland Cement* is a hydraulic mortar similar to the above. It is made from clay obtained from the valley of the Medway, and from chalk found in the same neighbourhood: it derives its name from the circumstance that in colour, when dry, it resembles



Portland stone. It is prepared by thoroughly grinding the clay and chalk with water, allowing them to deposit, then drying and burning the mixture until it undergoes slight vitrification; the mass is ground, and when mixed with a proper proportion of water, it forms a cement which possesses great hardness and tenacity; it expands as it solidifies.

The rapidity with which these different kinds of hydraulic limes set, varies considerably with their composition. If the clay do not exceed 10 per cent. of the mass, the mortar requires several weeks to harden. If the clay amount to from 15 to 25 per cent. it sets in two or three days, and if from 25 to 35 per cent. of clay be present, the solidification occurs in a few hours. The substance to which the term *Roman cement* is applied, is a lime of this latter description. Roman cement was originally prepared from nodules of septaria which occur in the bed of the Thames. It sets a few hours after the mixture with water has been effected, and it soon rivals stone in hardness. According to Meyer, the composition of the nodules employed in the preparation of the cement is the following:—

Matter soluble in acid 76.0	{	Carbonate of lime . . . . .	66.99
		"    magnesia . . . . .	1.67
		"    of iron . . . . .	6.95
		Alumina . . . . .	0.39
Insoluble in acid (Clay) 23.305	{	Silica . . . . .	16.89
		Alumina . . . . .	4.32
		Oxide of iron . . . . .	1.72
		Lime . . . . .	0.05
		Magnesia . . . . .	0.37

The cement obtained from the neighbourhood of Boulogne is almost identical in composition with the foregoing, and similar materials have been obtained in other countries, particularly in the beds of the Jurassic formation.

*Concrete* is a mixture of hydraulic mortar with small pebbles coarsely broken.

In order that hydraulic lime may properly harden, it must not be submerged till it begins to set; it should then be kept moist until it is quite hard, otherwise it always remains porous. Care must be taken in burning these limes not to subject them to too high a temperature, otherwise they become dead burnt, the silica and alumina combining with the lime in the furnace instead of the combination occurring when made into mortar. The success of the preparation of a hydraulic lime appears to depend upon the formation of a finely divided silica and alumina, uniformly disseminated through the mass. The occurrence of any vitrification of

the particles preventing their subsequent union with the hydrate of lime. The immediate cause of solidification in these hydraulic limes appears to be the formation of a hydrated compound of lime with the silica and alumina, but in process of time a silicate and aluminate of lime are formed.

(536) *Other uses of Lime.*—Lime is also largely employed as a manure, and it is particularly valuable upon very rich vegetable soils, such as those formed over peat bogs; its effects in these cases are partially due to the decomposition of the organic matter, which it renders soluble and capable of assimilation, while the lime itself is converted into carbonate. It has been found that limestone, containing much carbonate of magnesia, yields a lime unsuited to agricultural purposes: this is attributed to the fact that magnesia absorbs carbonic acid much more slowly than lime, and remains caustic for a longer period, in which state it appears to be injurious to the tender shoots of the young plants.

The strong affinity of lime for carbonic acid renders it a valuable material for separating this acid from the carbonates of potash and soda, which may thus be obtained in a caustic form. Its attraction for water furnishes a means of removing this liquid from many substances, such as alcohol, which retain it with considerable force; the finely powdered lime is mixed with the alcohol, and the mixture having been allowed to stand for a few days, with occasional agitation, is subjected to distillation: the anhydrous alcohol passes over, leaving the water combined with the lime. Lime is employed also as a direct chemical agent in the purification of coal-gas, and as a means of loosening the epidermis, and facilitating the removal of the hair from hides, as a preliminary to the process of tanning.

Binoxide of hydrogen forms an insoluble compound with lime, which precipitates in crystalline scales when the binoxide is poured into lime water: it is very unstable, and undergoes spontaneous decomposition at the temperature of the air. This substance is generally spoken of as *binoxide of calcium*.

(537) *Sulphides of Calcium.*—Calcium forms several compounds with sulphur.

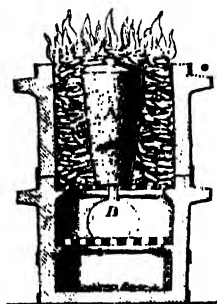
The *protosulphide of calcium*, ( $\text{CaS}$ ), *Eq. 36*, is procured by decomposing a mixture of sulphate of lime and charcoal by heat, as directed for sulphide of barium. It is very sparingly soluble in water, and is phosphorescent when newly prepared. This property was first observed by Canton, in an impure sulphide of calcium, which he obtained by calcining oyster shells in an open fire for half

an hour, then selecting the whitest and largest portions, and packing them with one-third of their weight of flowers of sulphur in a crucible with a luted cover; this was heated strongly for an hour: when cold, the crucible was broken, and the whitest pieces were placed in well-closed bottles.

By boiling slacked lime with excess of sulphur, a *pentasulphide of calcium* is obtained, and hyposulphite of lime is formed at the same time;  $3 \text{ CaO} + 12 \text{ S} = 2 \text{ CaS}_5 + \text{CaO}, \text{S}_2\text{O}_2$ .

(538) *Phosphide of Calcium*, ( $\text{Ca}_2\text{P}$ ); *Eg.* 72.—This compound presents some interest, from its affording the most convenient source of the phosphides of hydrogen (376). It is prepared by distilling phosphorus over lime heated to low redness: a mixture of phosphide of calcium and phosphate of lime is the result,  $7 \text{ P} + 14 \text{ CaO} = 2(2 \text{ CaO}, \text{PO}_5) + 5 \text{ Ca}_2\text{P}$  (P. Thénard). The most

FIG. 297.



convenient method of conducting the operation is shown in fig. 297. In the lower part of a narrow deep crucible, A, a hole is drilled for the reception of the neck of a flask, B, which is luted into the aperture; a quantity of dry phosphorus is placed in the flask, and the crucible is filled with quick lime, broken into fragments the size of a nut; a lid is then luted upon the top of the crucible. The upper part of the crucible is then raised to a red heat as quickly as possible by surrounding it with ignited charcoal, the lower part of the furnace having been filled with cold charcoal, to prevent the heat from reaching the phosphorus too rapidly; the phosphorus gradually volatilizes as the heat reaches it. If the heat be too high, the phosphorus distils over without combining with the calcium.

Phosphide of calcium is of a dull red colour, and is hard enough to strike fire with steel; it experiences no change in dry air or in oxygen at the ordinary temperature. At a high temperature it becomes partially decomposed by oxygen, chlorine, or hydrochloric acid; in a moist atmosphere it slacks, emits phosphuretted hydrogen, and crumbles to a brown powder. This powder, when thrown into water, or heated to  $212^\circ$ , evolves phosphuretted hydrogen, which is not self-lighting, and is mixed with free hydrogen.

Phosphide of calcium, in its unslacked form, is decomposed when thrown into water; phosphuretted hydrogen gas is evolved, and takes fire with the phenomenon already described (376); dilute acids produce its decomposition still more rapidly.

(539) *Chloride of Calcium*, ( $\text{CaCl}$ , 6 aq), *Eq.* 55.5 + 54, *Sp. Gr.* fused, 2.485, *cryst.* 1.680.—This salt is prepared by dissolving chalk in hydrochloric acid, evaporating to dryness, and fusing the residue at a red heat. By evaporation of its solution it may be obtained in striated prismatic four-sided crystals, with 6 equivalents of water; and if heated to  $300^{\circ}$  it forms a porous mass which still retains 2 equivalents of water; in this state it is well adapted for the desiccation of gases. It is an extremely deliquescent salt, is soluble in alcohol, and may be obtained from its alcoholic solution crystallized in rectangular plates, containing 2 equivalents of alcohol. Chloride of calcium absorbs ammonia rapidly, and forms a compound with 4 equivalents of the gas. A solution of the chloride, if boiled with quick lime and filtered while hot, deposits long, flat, thin crystals of a hydrated oxychloride, consisting of ( $\text{CaCl}$ , 3  $\text{CaO}$ , 15 aq), which are decomposed both by water and by alcohol.

*Fluoride of Calcium* ( $\text{CaF}$ , *Eq.* 39, *Sp. Gr.* 3.14) is an abundant mineral, well known as *fluorspar*, which occurs either massive or crystallized in forms allied to the cube. It is found accompanying the lead veins in Cumberland, Derbyshire, and Cornwall, and is met with in a variety of other localities, of various colours, most frequently blue, green, or white. Fluorspar is the principal source whence the compounds of fluorine are obtained. Fluoride of calcium, in minute quantity, is found in sea water (Dr. G. Wilson), and in many springs: it is a never-failing companion of phosphate of lime in the bones and teeth of animals, and indeed is always found to accompany phosphate of lime in the mineral kingdom also in small but variable quantities. Most varieties of fluorspar, when gently heated, become phosphorescent, emitting a pale green or violet light; if heated more strongly, the crystals decrepitate, and each fragment becomes enveloped for a few seconds in a beautiful halo of light. It loses this property after having been once heated; a phosphorescent fluor, dissolved in hydrochloric acid, and precipitated by ammonia, retains its power of emitting light when heated, but if it had been previously heated sufficiently to destroy the phosphorescence, this property is not restored by solution and reprecipitation.

Fluoride of calcium absorbs sulphuric acid if mixed with it at a low temperature, and forms a transparent, viscous mass, from which fumes of hydrofluoric acid are evolved by heating it to  $100^{\circ}$ . Fluorspar undergoes no change when heated with anhydrous sulphuric acid, but with dry boracic acid it yields borate of lime and borofluoric acid. Hydrochloric acid dissolves it in small quantity. When fused

with the alkalis, it undergoes no change: with the carbonated alkalis fluoride of the alkaline metal and carbonate of lime are formed. If heated with sulphate of lime, it fuses and forms a glass which is transparent when hot, but enamel white when cold. In proper proportions it often forms a valuable flux in smelting the ores of various metals, and hence the name *fluor* is derived.

(540) *Sulphate of Lime*, ( $\text{CaO}, \text{SO}_3$ ), *Eq. 68, Sp. Gr. 2.95: crystallized as gypsum* ( $\text{CaO}, \text{SO}_3, 2 \text{HO}$ ), *Eq. 68 + 18, Sp. Gr. 2.30.*—This compound occurs free from water in the mineral *anhydrite*, crystallized in rectangular prisms, which are found in the salt rocks of the Tyrol, and in Upper Austria; but it is much more abundant as a hydrate with 2 equivalents of water: it is then met with either in transparent flattened prisms, known as *selenite*, or still more frequently in a fibrous, granular, compact, or earthy form, constituting the different varieties of gypsum and alabaster. Sulphate of lime is a very common impurity in spring water. Such waters are termed *selenitic*; they deposit upon the interior of boilers in which they are used, a strongly adherent fur or crust, the composition of which is  $2(\text{CaO}, \text{SO}_3) \text{aq.}$

Sulphate of lime is produced whenever a strong solution of a salt of lime is precipitated by any sulphate, in which case it falls as a white voluminous sparingly soluble hydrate, which requires about 400 parts of water for its solution. When heated it loses its water, and, if the temperature be raised to bright redness, the anhydrous mass fuses, and may be obtained in crystals the same in form as those of anhydrite.

Gypsum constitutes a manure of considerable value when judiciously employed; but the most remarkable property of sulphate of lime, and that for which it is chiefly valued, is the power which the hydrated variety possesses, after it has been deprived of water by a heat not exceeding  $500^\circ$ , of again combining with water, and binding or setting into a hard mass. If the dry powder be made into a thin paste with water, the mixture becomes solid in a few minutes, expands considerably at the moment of solidification, and emits a considerable amount of heat: a combination of 2 equivalents of water with 1 of sulphate of lime occurs, and eventually it becomes as hard as the original gypsum. Gypsum which has been dried at this regulated temperature is converted into a white friable mass, which when ground to a fine powder is known in the arts under the name of *plaster of Paris*, from the circumstance of the mineral being extensively found in the environs of the French metropolis. It is however particularly worthy of observation, that if the sulphate be heated to redness, it becomes very much denser, assumes

a crystalline structure, and loses the power of setting or solidifying when mixed with water by recombining with the 2 equivalents it had lost.

Plaster of Paris is manufactured in large quantities for architectural purposes : it is also largely used in modelling, and in taking accurate copies of objects of every description. Suppose, for instance, it were desired to copy a medal : a raised rim of pasteboard is attached to the medal, which is anointed with a little oil, to prevent the plaster from adhering to its surface. The dried plaster is then mixed with water till it is of the consistence of thin cream, and is immediately applied carefully with a hair pencil to every part of the surface, so as to exclude air, after which a thicker cream is poured into the mould : in a few minutes the mass becomes solid, and the cast may be removed from the medal.

The addition of 1 or 2 per cent. of many salts, particularly of alum, of sulphate of potash, or of borax, confers upon gypsum some properties of considerable practical importance. Gypsum which has been thus treated will endure a dull red heat without losing its power of setting when mixed with water. It becomes much denser than ordinary plaster, and when mixed with water, sets in the course of a few hours and forms a hard material which takes a high polish. Keene's, Martin's, and Keating's cement are the names under which plaster so treated is known. *Stucco* consists of coloured plaster, mixed with a solution of size. The different colours exhibited by stucco are obtained by the admixture of oxides of iron and other metals. By friction its surface is susceptible of a high polish.

Sulphate of lime forms a double salt with sulphate of soda, which is found native under the name of *glauberite* ( $\text{NaO}, \text{SO}_3 + \text{CaO}, \text{SO}_3$ ) ; it is anhydrous, and nearly insoluble in water.

*Nitrate of Lime* ( $\text{CaO}, \text{NO}_3$  6 aq, *Eq.* 82 + 54) is a deliquescent salt, which crystallizes in long prisms ; when anhydrous, it emits light if gently heated. It is soluble in alcohol.

(54) *Carbonate of Lime* ( $\text{CaO}, \text{CO}_2$ ) ; *Eq.* 50 ; *Sp. Gr.* of *Iceland spar*, 2.72, of *Aragonite*, 2.97. This substance is one of the most abundant components of rocks and minerals. In the amorphous condition, it forms the different varieties of limestone, *oolite*, chalk, and calcareous marl ; it is the principal constituent of corals, of the shells of fishes, and of the eggshells of birds ; it also enters in greater or less quantity into the bones of animals. In minute granular crystals it forms the different kinds of marble, and it is found in a greater variety of regular crystalline forms than any other known compound. Its primary form is a rhombo-

hedron, as is seen in Iceland spar, but it also occurs in the incompatible form of aragonite, in six-sided prisms, and is consequently dimorphous. Aragonite is isomorphous with carbonate of strontia, and its crystals not unfrequently contain small quantities of this mineral, the occurrence of which it is supposed may assist in determining the assumption of the prismatic form by the carbonate of lime. When aragonite is heated it falls to powder, and the grains are stated to assume the form of minute rhombs. Carbonate of lime is produced whenever a salt of lime is precipitated by the addition of an alkaline carbonate, and if the solutions are mixed at the boiling point, the carbonate falls in microscopic crystals, having the form of aragonite.

It is sometimes necessary to obtain a perfectly pure carbonate of lime; for this purpose solution of nitrate of lime may be mixed with an excess of lime water, which precipitates oxide of iron and other metallic oxides; the filtered solution is decomposed by the addition of a mixture of ammonia and sesquicarbonate of ammonia; the precipitate is washed thoroughly, then dried and heated to low redness.

Carbonate of lime is decomposed by a red heat, if the acid can freely escape; but in close vessels it fuses without undergoing decomposition, and on cooling forms a granular crystalline mass, like marble.

A combination of carbonate of lime and soda, insoluble in water, was found at Merida, in South America, and called *Gay Lussite* ( $\text{CaO}, \text{CO}_2, \text{NaO}, \text{CO}_2, + 6 \text{ aq.}$ ). *Barytocalcite* ( $\text{CaO}, \text{CO}_2 + \text{BaO}, \text{CO}_2$ ) is a native double carbonate of lime and baryta, which crystallizes in oblique prisms.

(542) *Calcareous Waters*.—Carbonate of lime dissolves in pure water to the extent of rather more than 2 grains in 1 gallon, but it is freely taken up by water charged with carbonic acid, and is deposited again in anhydrous crystals as the gas escapes. In this way enormous masses of crystallized carbonate of lime are formed. In the limestone hills of Derbyshire, and in various other localities, caverns occur in which this phenomenon is perpetually exhibited; water charged with carbonic acid and carbonate of lime makes its way through the roof of the cavern, where as the carbonic acid gradually escapes, the carbonate of lime is deposited in dependent masses, like icicles, termed stalactites; whilst the water falling on the floor of the cavern before it has parted with all its excess of carbonic acid and dissolved limestone, deposits a fresh portion of the crystalline matter; and thus a new growth, or stalagmite, gradually

rises up to meet the stalactite which depends from the roof: in this way a natural pillar of crystallized carbonate of lime is formed.

It is in a similar manner that the calcareous deposits from the lakes of volcanic districts are produced. These deposits, when porous, have received the name of *tufa*; when more compact they are termed *travertine*. Travertine is formed abundantly in many of the Italian lakes; it was highly valued for architectural purposes by the Romans, as it was a material easily wrought, and possessed great durability and beauty.

Many spring waters contain carbonate of lime held in solution by carbonic acid: when the water is boiled this acid is expelled, and the carbonate is deposited, forming a lining more or less coherent upon the sides of the vessel. In steam boilers this becomes a serious evil: it is effectually prevented by the addition of a small quantity of sal ammoniac to the water; carbonate of ammonia is formed, and volatilizes, while chloride of calcium remains dissolved.

Dr. T. Clark has introduced a plan for softening such calcareous waters, by removing the carbonic acid from them, and causing the precipitation of the carbonate of lime by thus depriving it of its solvent. This method consists essentially in the addition of milk of lime to such waters, until the water gives a very faint brown tinge on testing it with a solution of nitrate of silver; this reaction indicates that a slight excess of lime has been added, which occasions a precipitate of brown hydrated oxide of silver. In this operation the lime combines with the excess of carbonic acid in the water; the carbonate of lime thus formed, being insoluble, precipitates along with the portion of carbonate of lime previously held in solution by the carbonic acid. After the lapse of twenty-four hours the water becomes perfectly bright and clear. If colouring or organic matters be present in the water, a considerable portion of both go down with the chalk. In applying this process upon a large scale, it is found advantageous to add a slight excess of lime in the first instance, and afterwards to destroy this excess by a fresh addition of unlimed water. The carbonate of lime then separates in granular crystals, which speedily subside. These crystals are formed much more slowly if the lime be not first in slight excess.

(543) *Building Materials*.—Carbonate of lime forms the basis of some of the materials most highly prized for building purposes, besides furnishing the costly varieties of marble used for interiors. The oolites, such as those from the Isle of Portland and the neighbourhood of Bath, resist the weather admirably; they admit of



being readily fitted and cut, and yet possess considerable hardness. Many shelly limestones are also well adapted for these purposes. Where elaborate carving is required, a well crystallized magnesian limestone (or double carbonate of lime and magnesia), such as that employed in the new Houses of Parliament, is preferred; it is very close and compact, sufficiently soft to be easily sculptured, but retains a sharp outline. Many fine-grained, porous calcareous and magnesian stones have the inconvenience of splitting into flakes after a few years' exposure; this generally occurs from the absorption of water, and its expansion when the moisture thus absorbed becomes frozen during winter. A simple and ingenious mode of ascertaining whether a building stone is liable to this defect was invented by Brard:—it consists in taking a smoothly cut block of the stone, one or two inches in the side, and placing it in a cold saturated solution of sulphate of soda. The temperature of the solution is gradually raised to the boiling point, and then the stone is left to cool in the liquid. When cold, it is suspended over a dish, and plunged for a few moments in a cold saturated solution of the sulphate of soda every day for a week or a fortnight, and is then again freely suspended in the air. The sulphate of soda crystallizes in the pores of the stone, and splits off fragments of it. A similar experiment is made upon a stone which is known to be free from this defect. By the comparative weight of these fragments in the two cases the tendency of the stone to the defect in question may be estimated.

A valuable report upon the composition and quality of various kinds of building stones was made to the Government in 1839, upon the occasion of the rebuilding of the Houses of Parliament.

The other varieties of building stones are mostly siliceous. To this class belong all the sandstones, which consist chiefly of grains of silica united by a cement more or less ferruginous. The durability of the stone depends mainly upon the character of this uniting material. Many igneous rocks, such as porphyry, basalt, and more especially granite, are also used for building purposes; but from their hardness, they are seldom wrought, except when, as in quays, bridges, or causeways, the constant wear is unusually great, and where softer though less expensive materials would soon be destroyed.

(544) *Phosphates of Lime*.—The most remarkable of the phosphates of lime is that known as the bone phosphate ( $3 \text{ CaO}, \text{PO}_5$ ), from its forming the principal earthy constituent of the animal skeleton. It is easily procured by adding chloride of calcium, drop by drop, to a solution of phosphate of soda in excess, when it falls as a gelatinous precipitate. It may also be obtained from calcined bones by digesting them in nitric acid, and precipitating the

filtered solution by caustic ammoniac. This phosphate is insoluble in water, but is readily dissolved by acetic, and the stronger acids. It occurs native as a white amorphous mineral, known under the name of *phosphorite*.

. A tribasic phosphate of lime occurs naturally crystallized in hexagonal prisms, which, when colourless, are called *apatite*; when of a green colour it is termed *mororite*; in these minerals the phosphate is associated with variable quantities of fluoride of calcium. When rhombic phosphate of soda is added drop by drop to an excess of chloride of calcium, a semi-crystalline precipitate falls, which according to Berzelius, consists of  $(2 \text{ CaO}, \text{HO}, \text{PO}_5, 3 \text{ aq})$ . Several other phosphates of lime may be formed, corresponding in composition to the various phosphates of soda.

(545) CHARACTERS OF THE SALTS OF LIME—The salts of lime are colourless. They give no precipitate with *ammonia*, but yield a white precipitate of carbonate of lime, with the *alkaline carbonates*. Solution of *sulphate of lime* produces no precipitate; the lime salts are thus distinguished from those of baryta and strontia: they yield no precipitate with *hyposulphate of ammonia*. *Oxalate of ammonia*, even in very dilute solutions of lime, throws down a white oxalate of lime, which dissolves in nitric and hydrochloric acids.

In the determination of lime for analytical purposes the oxalate is the precipitate usually employed; but before weighing, it is heated to dull redness, so as to convert the oxalate into carbonate of lime: 100 parts of carbonate of lime contain 44 parts of carbonic acid and 56 of lime. If no other base be present, lime may also be estimated in the form of sulphate. If the lime be not already in the state of sulphate, the salt is heated with an excess of sulphuric acid, and ignited; when cold, it is weighed: 100 grains of sulphate of lime contain 41.17 of lime.

#### § IV. MAGNESIUM.

*Symbol*, Mg; *Equivalent*, 12; *Specific Gravity*, 1.7.

(546) MAGNESIUM is usually classed with those metals the oxides of which furnish the alkaline earths, but it is much more analogous to zinc in its properties than to any other element. Magnesium is an abundant ingredient of the crust of the earth. It is found in large quantities as a double carbonate with lime, forming *magnesian limestone*, or *dolomite*. It is contained abundantly in sea water as chloride, and in many springs as

sulphate. It likewise enters more or less extensively into the formation of many rocks, and of a great variety of minerals. Bussy obtained it in the metallic form by heating its anhydrous chloride with potassium in a porcelain or platinum crucible. When cold, the contents of the vessel were digested in cold water, by which the chloride of potassium and undecomposed chloride of magnesium were dissolved out. The metal was left as a grey powder, which could be melted into globules.

Bunsen (Liebig's *Annalen*, lxxxii. 137) prepares magnesium by the electrolytic decomposition of the chloride of magnesium, which he melts in a deep covered porcelain crucible, divided by a vertical diaphragm of porcelain, which extends half way down the crucible; the electrodes are made of carbon, and are introduced through two openings in the lid, the negative electrode being notched to receive the reduced magnesium which lodges in the cavities: the crucible is brought to a red heat, and is filled with the melted chloride, which then is readily decomposed by 10 cells of the zinc-carbon battery (233). The principal difficulty in this operation arises from the small density of the reduced metal, which rises to the surface of the fused salt, and is liable to reoxidation.

Magnesium is a malleable metal of the colour of silver, and a density of 1.7. Its fracture appears sometimes crystalline, at other times fibrous. It has about the same degree of hardness as calc spar. At a moderate red heat it may be melted. At ordinary temperatures, it undergoes no change in dry air, but in a moist atmosphere it becomes slowly oxidized. When ignited in dry air, or in oxygen gas, it takes fire and becomes oxidized, emitting a light of dazzling brilliancy; the magnesia which is produced exhibits no signs of fusion. Magnesium is but slowly acted upon by cold water, but it is rapidly dissolved if the water be slightly acidulated. When thrown into strong hydrochloric acid it bursts into flame; yet a mixture of concentrated sulphuric and fuming nitric acid has no action upon it in the cold. When heated in chlorine and in the vapour of bromine, of iodine, or of sulphur, it burns brilliantly.

(547) *Magnesia*, ( $MgO$ ); *Eq.* 20; *Sp. Gr.* 3.6.—The only known oxide of magnesium is a bulky, white, tasteless, infusible, and nearly insoluble powder which when placed upon moistened turmeric paper turns it distinctly brown. It is usually procured by strongly igniting the artificial carbonate in a crucible, but it may also be obtained by ignition of the nitrate of magnesia; in this case it assumes a much denser form. Magnesia, when mixed with water, gradually

combines with it, and forms a hydrate ( $\text{H}_2\text{O}$ ,  $\text{MgO}$ ), which slowly absorbs carbonic acid from the air: no sensible elevation of temperature occurs during the process of hydration. A native hydrate of similar composition occurs in crystalline scales.

*Sulphide of Magnesium* ( $\text{MgS}$ ), *Eq.* 28.—This compound is but sparingly soluble in water. It may be obtained by precipitating a boiling solution of sulphate of magnesia by sulphide of potassium, when it falls as a white mucilaginous mass.

(548) *Chloride of Magnesium* ( $\text{MgCl}$ , *Eq.* 48, *Sp. Gr.* 2.177) is obtained by dissolving 1 part of magnesia in hydrochloric acid, and adding 3 parts of sal ammoniac in solution, the mixture is evaporated to dryness; by this means a double chloride of magnesium and ammonium is formed ( $\text{NH}_4\text{Cl}$ , 2  $\text{MgCl}$ ), which may be evaporated without loss of acid, whilst the solution of mere chloride of magnesium is partially decomposed during evaporation. When the double salt is ignited in a covered crucible, the sal ammoniac is expelled, and pure chloride of magnesium remains. At a red heat it fuses to a transparent liquid, which forms a silky looking mass of confused crystals on cooling. Chloride of magnesium is deliquescent, and gives out heat whilst dissolving in water; by evaporation at a low temperature it may be obtained in crystalline needles which contain 6 equivalents of water. It is soluble in alcohol: it forms double chlorides with the chlorides of the alkaline metals.

(549) *Sulphate of Magnesia*, ( $\text{MgO}$ ,  $\text{SO}_3$ ,  $\text{H}_2\text{O}$ , 6 aq); *Eq.* 60 + 63; *Sp. Gr. anhydrous*, 2.706, *cryst.* 1.660.—This is the most important salt of magnesia. It is made in very large quantities from sea water, either by precipitating the magnesia by means of lime, and then dissolving it in sulphuric acid, or by first crystallizing out the greater part of the common salt, and treating the mother liquor with sulphuric acid; by evaporation, crystals of the sulphate are obtained. The sulphate is also procured in considerable quantities from magnesian limestone: the rock is burnt, slaked, and largely washed with water to remove part of the lime; it is then treated with sulphuric acid, and the sulphate of magnesia is separated from the sparingly soluble sulphate of lime by solution and recrystallization. Sulphate of magnesia is a common ingredient in mineral waters. Its trivial name of Epsom salts is derived from the circumstance of its being largely contained in many springs in the neighbourhood of Epsom, from the waters of which it was at one time obtained.

Sulphate of magnesia dissolves in 3 times its weight of water

at  $60^{\circ}$ , and  $1\frac{1}{2}$  at  $212^{\circ}$ . Its solution has a bitter disgusting taste. It crystallizes readily in right rhombic prisms, which are slightly efflorescent: when heated moderately, they lose their water of crystallization; if the heat be intense and long continued, a part of the acid also escapes. Crystallized sulphate of magnesia loses 6 equivalents of its water at a temperature below  $300^{\circ}$ , but it retains 1 equivalent even at  $400^{\circ}$ . This last equivalent may be displaced by an equivalent of an anhydrous salt, such as sulphate of potash, with which it forms a double salt, possessed of the same crystalline form as sulphate of magnesia ( $\text{MgO}, \text{SO}_5 + \text{KO}, \text{SO}_3 + 6 \text{ aq}$ ) of sp. gr. 2.076.

*Nitrate of Magnesia* ( $\text{MgO}, \text{NO}_5 + 6 \text{ aq}$ , Eq. 74 + 54) Sp. Gr. 1.464), is deliquescent, and crystallizes with difficulty.

(550) *Carbonate of Magnesia* ( $\text{MgO}, \text{CO}_2$ , Eq. 42) occurs native as a white hard mineral, called *magnesite*. It is procured by precipitating a boiling solution of a salt of magnesia by carbonate of potash, and dissolving the precipitate in carbonic acid water; as the gas escapes, the salt is deposited as a terhydrate, in transparent hexagonal prisms ( $\text{MgO}, \text{CO}_2, 3 \text{ aq}$ ); by exposure to air these crystals effloresce and are converted into a protohydrate ( $\text{MgO}, \text{CO}_2, \text{HO}$ ).

The common white magnesia of the shops is made by precipitating a boiling solution of sulphate of magnesia by a hot solution of carbonate of soda. The sulphate of magnesia is allowed to remain slightly in excess, otherwise the precipitate retains a little carbonate of soda. It is deposited as a white, light, bulky powder, which is composed of hydrate of magnesia ( $\text{HO}, \text{MgO}$ ) combined with a quantity of hydrated carbonate ( $\text{MgO}, \text{CO}_2, \text{aq}$ ) which may vary from 2 to 4 equivalents; it is very sparingly soluble in water.

*Dolomite*, when its structure is crystalline, usually consists of carbonate of magnesia and carbonate of lime in the proportion of 1 equivalent of each ( $\text{MgO}, \text{CO}_2 + \text{CaO}, \text{CO}_2$ ), though sometimes the carbonate of lime considerably exceeds 1 equivalent.

Mr. Pattinson has introduced a process by which a very pure carbonate of magnesia is manufactured from dolomite. In this operation the mineral is finely ground and sifted, and exposed to a red heat for 2 or 3 hours, by which the carbonate of magnesia is decomposed. It is then introduced into a strong iron cylinder, lined with lead, where it is mixed with water, and carbonic acid gas is forced in under a pressure of 5 atmospheres till it ceases to be absorbed; the carbonate of magnesia dissolves as

bicarbonate, leaving the carbonate of lime: the clear liquid, when boiled, deposits the carbonate of magnesia, which is drained and dried in a stove at a low temperature.

By mixing a solution of nitrate of magnesia with an excess of a saturated solution of bicarbonate of potash, and allowing the solution to stand some days, a remarkable double salt is deposited in regular crystals, composed of  $2 (\text{MgO}, \text{CO}_2) + (\text{KO}, \text{HO}, 2 \text{CO}_2) + 8 \text{aq}$ , but which is decomposed by re-dissolving it in water. The corresponding salt of soda is more stable.

A native *Borate of Magnesia*,  $2 (\text{MgO}, \text{BO}_3) + (\text{MgO}, 2 \text{BO}_3)$ , named *boracile*, is found crystallized in cubes; it is rendered electric by heat.

(551) *Silicates of Magnesia*.—Silica and magnesia may be artificially combined in many proportions. A large number of minerals are formed, either wholly or partially, of the silicates of magnesia. *Olivine*, or *chrysolite*,  $2 (\text{MgFe})\text{O}, \text{SiO}_2$ , is a crystallized mineral, usually of a green colour, obtained from basaltic and volcanic rocks; it frequently accompanies masses of meteoric iron. *Talc* is a very soft slaty mineral, which has a formula  $2(\text{MgO}, \text{SiO}_2) + 2 \text{MgO}, 3 \text{SiO}_2$ . *Steatite*, or soapstone, is  $\text{MgO}, \text{SiO}_2 + 2 \text{MgO}, 3 \text{SiO}_2$ . *Picrosmine* is the neutral hydrate  $2(\text{MgO}, \text{SiO}_2) \text{aq}$ . *Meerschaum* is another hydrated silicate, of which the formula is  $2 \text{MgO}, 3 \text{SiO}_2 + 4 \text{aq}$ . *Serpentine*,  $2[(\text{MgFe})\text{O}, \text{SiO}_2] + \text{MgO}, 2 \text{aq}$ , is another hydrated silicate of magnesia, in which a portion of the magnesia is often displaced by protoxide of iron. Serpentine frequently occurs in compact masses, which take a high polish, and from the beauty of its variegated colours, it is often employed for ornamental purposes. It is readily attacked by acids, and occurs in sufficient abundance to be employed as a source of the salts of magnesia.

The double silicates of magnesia are still more numerous. *Augite* or *pyroxene* is one of these; it is a crystalline mineral, often found in basalt and lava, and is a silicate of lime and magnesia, portions of which are often displaced by protoxides of iron and manganese  $(\text{CaMgFeMn}) \text{O}, \text{SiO}_2$ . *Hornblende* or *Amphibole* is a silicate and aluminate of magnesia, lime, and protoxide of iron, with a variable proportion of the fluorides of calcium and potassium,  $3 [(\text{MgCaFe}) \text{O}, \text{SiO}_2] + 2 (\text{MgCaFeMn}) \text{O}, 3 \text{SiO}_2 + x (\text{KCa}) \text{Fl}$ . It occurs sometimes in dark green or black crystals, at other times massive, disseminated through many rocks, such as syenite and porphyry, and frequently in basalt and lava. *Asbestos* and *Amianthus* commonly consist of a fibrous variety of amphibole.

(552) *Triphosphate of Magnesia and Water*  $(\text{H}_2\text{O}, 2 \text{MgO} + \text{PO}_5$

+ 14 aq) is an efflorescent, sparingly soluble salt, which crystallizes in fine acicular tufts when a solution of a magnesian salt is mixed with the solution of the common phosphate of soda.

*Triphosphate of magnesia and ammonia*, ( $2 \text{ MgO}, \text{NH}_4\text{O}, \text{PO}_5$ , 12 aq; *eq.* 138+108,) or *triple phosphate*, as it was formerly called, is a more important compound than the foregoing. It is prepared by mixing phosphate of soda, mingled with chloride of ammonium, with a salt of magnesia; by agitation this compound is deposited in minute crystalline grains; it furnishes a most delicate test of the presence of magnesia; it is insoluble in water containing free ammonia or muriate of ammonia, but it is taken up in appreciable quantities by pure water. It is frequently met with as a constituent of urinary calculi, both in man and in the lower animals.

Phosphate of magnesia and ammonia is readily soluble in acids; ammonia precipitates it from such solutions unchanged; when ignited it parts with its water and ammonia, and glows like alumina and zirconia when ignited. This ignited residue contains 35.7 per cent. of magnesia, and 64.3 of phosphoric acid. It is frequently employed for the determination of the amount of magnesia.

(553) CHARACTERS OF THE SALTS OF MAGNESIA.—The salts of magnesia are colourless, and have a bitter taste. Many of the magnesian minerals possess a silky lustre, and feel unctuous to the touch. They may be recognised *before the blowpipe*, by assuming a pink tinge when heated with nitrate of cobalt.

In solution, they give no precipitate with the *alkaline bicarbonates* till boiled; but a white basic carbonate of magnesia when mixed with a neutral *carbonate of potash or soda*, unless a salt of ammonia be present, which interferes with the precipitation. *Phosphate of ammonia* gives with them a white crystalline granular precipitate of double phosphate of magnesia and ammonia, which is easily soluble in acids. *Oxalate of ammonia*, mixed with sal ammoniac, gives no precipitate with the magnesian salts, neither do the *soluble sulphates*. The *fixed alkalis* throw down a white gelatinous hydrate of the earth, which is insoluble in excess of the precipitant. *Lime water* produces a similar precipitate. *Ammonia* produces but a very incomplete precipitation of magnesia from its solutions; the gelatinous precipitate which it occasions redissolves on the addition of a solution of hydrochlorate of ammonia, and a double salt of magnesia and ammonia is formed.

(554) CHARACTERS OF THE METALS OF THE FIRST GROUP (the

alkalies).—The salts of these metals when in solution are distinguished by the following characters.

1. By the absence of any precipitate on the addition of a solution of carbonate of potash, or of soda: in the case of lithia, if the salt exceed two per cent. of the solution, a precipitate of carbonate of lithia is liable to occur.

2. By the absence of any precipitate when sulphuretted hydrogen or hydrosulphate of ammonia is added to the solution.

3. By the occurrence of a precipitate with bichloride of platinum in the case of salts of ammonium or of potassium; and by the formation of prismatic crystals of the double chloride of sodium and platinum when evaporated in the presence of salts of soda.

(555) *Estimation of Potash and Soda.*—If the relative proportions of the potash and soda be not required, their combined weight is usually ascertained in the form of sulphates. They may in most cases be readily obtained in this condition by treating the solution with sulphuric acid, evaporating to dryness, and fusing the mass in a platinum crucible in which a fragment of carbonate of ammonia is suspended. The excess of sulphuric acid is thus readily dissipated, and the amount of the acid combined with the potash and soda is determined by precipitation with chloride of barium. When ammonia is present with salts of potash and soda, its amount may be determined by distilling off the ammonia in the manner already described (522).

In order to determine the quantity of potash and soda in a mixture of the salts of the two bases, they should be converted into the state of chlorides, and heated to low redness to expel moisture and all ammoniacal salts, allowed to cool, and weighed; a certain proportion of these mixed chlorides (ten or twelve grains will suffice) is then mixed with an excess of the bichloride of platinum, evaporated to dryness over a steam bath, and the excess of bichloride of platinum and chloride of sodium removed by washing with alcohol of specific gravity 860. The crystalline residue is collected on a filter and weighed. One hundred parts contain 30.53 of chloride of potassium. The quantity of chloride of sodium is obtained by deducting the weight of the chloride of potassium from that of the mixed chlorides employed.

(556) The conversion of the alkaline bases into the condition of chlorides, previous to precipitation by the bichloride of platinum, if they are not already in that form, is rather troublesome. They may be first converted into sulphates by evaporating the solution with a slight excess of sulphuric acid and igniting the residue;



the sulphates thus obtained are to be dissolved in water and mixed with solution of chloride of barium in slight excess. The sulphuric acid is thus precipitated as sulphate of baryta, and the alkalies are converted into chlorides; but the excess of baryta in the liquid must still be got rid of. A mixture of caustic ammonia and of the sesquicarbonate of ammonia is therefore added to the solution after it has been filtered from the sulphate of baryta. The excess of baryta is thus thrown down as carbonate, and the carbonate of baryta may then be removed by filtration. Once more the solution is evaporated to dryness in a platinum dish, and the residue gently ignited to expel the ammoniacal salts. The remaining mass now contains nothing but the mixed chlorides of sodium and potassium.

(557) CHARACTERS OF THE METALS OF THE SECOND GROUP (the Alkaline Earths).—

1. The salts of these metals when in solution give a white precipitate on the addition of solution of carbonate of soda or of potash.

2. They yield no precipitate with hydrosulphate of ammonia or with sulphuretted hydrogen.

3. Lime water occasions no precipitate except in cases in which the magnesian salts are present, or in which the solution contains free carbonic acid.

(558) *Separation of the Alkaline Earths from the Alkalies.*—Supposing a solution to contain salts of the alkalies and of the alkaline earths, the quantities of each base may be determined in the following manner:—an excess of a mixture of ammonia and sesquicarbonate of ammonia is added to the solution, and the liquid is evaporated to dryness; the ammonia thus combines with the acid previously in union with the earths, whilst the carbonic acid converts the earths into carbonates. The dry residue is then washed with water, which dissolves out the alkaline salts, and from this liquid the proportions of potash and soda can be ascertained in the manner already described (555). A little magnesia is apt to accompany the alkaline salts: its presence may be detected and its quantity determined by the addition of lime water to the solution; hydrate of magnesia is precipitated, and may be collected, weighed, and added to the amount obtained from the portion which was insoluble in water. The precipitation must be effected in a stoppered bottle, to exclude the carbonic acid of the atmosphere, which would precipitate a portion of lime with the magnesia. The excess of lime may be got rid of

by the addition of oxalic acid, which occasions a precipitate of oxalate of lime that can be separated on a filter, but need not be weighed. The earthy carbonates must now be dealt with in the following manner:—

(559) *Separation of Baryta, Strontia, Lime, and Magnesia from each other.*—The alkalis having been separated in the manner just described, the carbonates of the earths which in the preceding operation did not dissolve in water are taken up with dilute nitric acid, and the liquid is largely diluted. Sulphuric acid is then added as long as it occasions a precipitate.

If the liquid originally contained no alkaline salts it will not be necessary to convert the earths into carbonates, but the solution may be simply diluted, acidulated with nitric acid, and mixed with sulphuric acid, as before.

This precipitate may consist of the sulphates of baryta and of strontia. It must be collected, washed with boiling water and weighed, then fused with thrice its weight of carbonate of soda, by which it will be decomposed; double decomposition occurs, carbonates of baryta and strontia, and sulphate of soda being formed. The carbonates of baryta and strontia, being insoluble, are separated from the soluble sulphate of soda by washing, and the carbonates of the two earths are converted into chlorides by the action of dilute hydrochloric acid. The chlorides of barium and strontium are evaporated to dryness, weighed, and may then be separated with tolerable exactness by the action of alcohol, which dissolves the chloride of strontium, but leaves that of barium untouched.

The acid liquid from which the baryta and strontia have been separated is rendered slightly alkaline by ammonia, and the lime precipitated as oxalate, by means of oxalate of ammonia: this precipitate, after being well washed, is heated to dull redness, and is estimated as carbonate of lime.

The filtrate, which may still contain magnesia, is mixed with phosphate of soda, briskly stirred, and allowed to stand for twelve hours, to give time for the granular crystalline phosphate of magnesia and ammonia to subside: it is collected on a filter, washed with water which contains free ammonia, and estimated after ignition as pyrophosphate of magnesia.

(560) It will generally be found more convenient in separating the alkaline earths from the alkalis, in the first place to precipitate the baryta and strontia by sulphuric acid from the dilute acidulated solution; then to neutralize by ammonia, and separate the lime by the addition of oxalate of ammonia; to evaporate the

solution containing magnesia and the alkalis to dryness; then to redissolve the residuc in water, and separate the whole of the magnesia at once by the addition of lime water in a stoppered bottle, in the manner already described.

Certain precautions in manipulation are required in transferring a solution to a filter, in order to avoid loss. In pouring a liquid from one vessel to another, a glass rod should be moistened with distilled water and brought against the edge of the vessel from which the liquid is to be poured, as shown in fig. 298. By this means, when the pouring is ended, if the rod be still kept in contact with the edge,

FIG. 298.



the last drop is prevented from running down the outside of the jar or basin: the rod may then be placed in the vessel until a similar operation is again required. After the whole of the liquid has been poured off, the portion which adheres to the rod and to the sides of the vessel is washed down by a jet of water from the washing bottle, fig. 299; and the washings are added to the rest of the decanted liquid.

(561) In washing precipitates, the use of a flask provided with

FIG. 299.



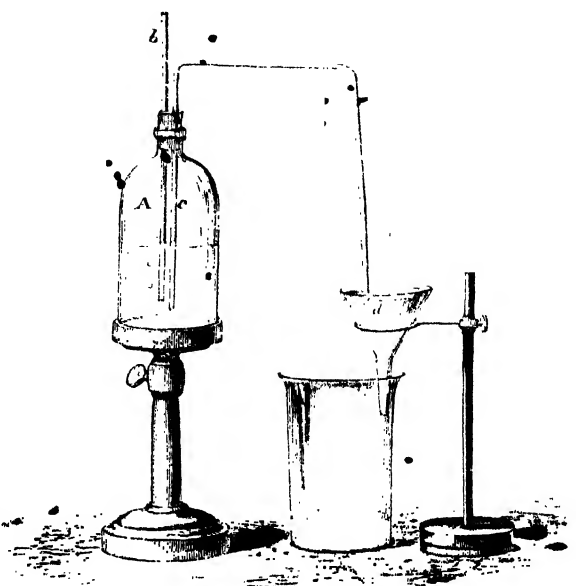
two tubes passing through the cork, as represented in fig. 299, facilitates the operation. The tube, *a*, passes just through the cork; the longer tube, *b*, reaches almost to the bottom of the flask; it terminates at *c* in a fine orifice; on forcing air from the lungs through the tube, *a*, the water is expelled at *c*, and may be directed upon the filter.

It is necessary that the filter should fall completely within the funnel, and that before any of the liquid for filtration is poured into it, the paper, after it has been placed in the funnel, should be moistened

with distilled water. In washing a precipitate, the stream of water should be directed upon the upper edges of the filter, so as to wash down the saline particles, which, by evaporation of the liquid, have a tendency to accumulate there as the solution rises under the influence of capillary action.

In cases where gelatinous precipitates, like oxide of iron, or alumina, are to be washed continuously for a long period, a simple contrivance by Gay Lussac will be found very useful; it is merely a bottle of distilled water, *A*, fig. 300, which by means of a syphon, supplies the water at a regulated level in the funnel, *d*; *b* represents a tube open at both ends, which reaches nearly to the bottom of the bottle, *A*; *c* is a syphon with limbs of equal length, which

FIG. 300.



passes a little deeper into the bottle than *b*; the limb which dips into the funnel has its lower extremity a little recurved, to direct the pure water upwards. The funnel, *d*, is placed so that the level of the filter shall be a little above that of the lower end of *c*. Under these circumstances the filter can never overflow. As soon as the surface of the liquid in the funnel falls just below the level of the lower extremity of *b*, the syphon carries over a small quantity of water, and bubbles of air rise in the bottle, *A*, to supply its place. This process goes on continuously as the water flows from the filter until *A* is empty. In order to ascertain whether a precipitate has been sufficiently washed, a drop of the liquid which passes through is evaporated on a slip of glass: it ought to leave no appreciable stain or residue.

In collecting a precipitate from a filter, the paper should be dried thoroughly; after which the portion that can be readily detached from the paper should be allowed to fall into the platinum or porcelain capsule in which it is intended to perform the ignition. The capsule is to be placed upon a smooth sheet of paper, and the filter being held at one corner with a pair of forceps, is burned in

such a way that the ashes shall fall into the platinum capsule: any particles of ash which may fall upon the paper are carefully transferred to the capsule.

It must not be forgotten that filtering paper itself leaves traces of ash when burnt; the amount of which in good specimens should not exceed about 3 grains in 1000. Before using any paper for the purposes of analysis the quantity of ash which a given weight of it affords when burnt must be ascertained. In each analytical experiment the weight of the filter employed being approximatively known, it is easy to estimate the amount of ash which it would yield (at most but a few-hundredths of a grain) and to deduct this from the gross weight of the precipitate.

## CHAPTER XIII.

### GROUP III.—METALS OF THE EARTHS.

#### § I. ALUMINUM.

*Symbol* Al; *Equivalent* 13.67; *Specific Gravity*, 2.5 to 2.67.

(562) THE pure earths are white, insipid, insoluble compounds, the oxides of metals which possess a high affinity for oxygen. With the exception of cerium, and lantanium, which, with didymium, would probably be referred with greater propriety to the next group, a single oxide only of each metal of this class is known.

(563) Of these metals the most abundant and important is aluminum, which derives its name from alum, into the composition of which it enters. Indeed, alumina (the oxide of aluminum) constitutes about 10 per cent. of this salt.

The properties of aluminum were first investigated by Wöhler, who procured it by decomposing chloride of aluminum in a porcelain or platinum tube by means of potassium. He obtained it first as a steel-grey powder, which is gradually oxidized by boiling water, and more rapidly by alkaline solutions. When it is heated in this form in oxygen gas, it takes fire and burns with a vivid light, emitting so intense a heat as to fuse the alumina, which forms a yellowish mass, in colour and hardness resembling native crystallized alumina as it exists in corundum.

At a subsequent period Wöhler obtained the metal in mal-

leable globules, resembling tin in appearance, of specific gravity varying between 2.5 and 2.67, fusible before the blowpipe, and unchanged by exposure to air.

The methods of preparing it have been recently simplified by Bunsen (Poggend. *Annal.*, xcii. 648) and by Deville (*Ann. de Chimie*, III. xliii. 5). Bunsen obtains aluminum by the electrolytic decomposition of the double chloride of sodium and aluminum ( $\text{NaCl}$ ,  $\text{Al}_2\text{Cl}_3$ ). This salt melts at about  $356^\circ \text{F}$ ., and readily furnishes aluminum by a process similar to that already described in the case of magnesium: but as the aluminum is heavier than the fused salt, it is more easily collected than magnesium.

M. Deville prepares aluminum in the following manner: Into a wide tube of hard glass an inch or an inch and a half in diameter, about half a pound of dry chloride of aluminum is introduced, and kept in its place by plugs of asbestos; a current of dry hydrogen, perfectly free from air, is transmitted, and the chloride of aluminum is very gently heated; in this way traces of hydrochloric acid and chlorides of sulphur and silicon are expelled.

Three or four small porcelain trays, each containing 40 or 50 grains of sodium, freed from adhering naphtha by pressure between folds of blotting paper, are then introduced into the tube; the current of hydrogen is still maintained, and heat is applied to the part of the tube which contains the sodium. This end of the tube must be slightly elevated, in order to prevent the melted chloride of aluminum from running down upon the sodium; in which case the heat emitted is so intense as to crack the tube.

When the sodium is melted, the chloride of aluminum is gradually distilled over by the application of a regulated heat, and is reduced with vivid incandescence. A double chloride of aluminum and sodium forms in the porcelain trays around the reduced aluminum. These trays and their contents are withdrawn when cold from the glass tube and placed in a porcelain tube through which a current of hydrogen is transmitted, whilst the tube is raised to a bright red heat; the aluminum fuses into globules in the porcelain trays; and by fusing it once more in a porcelain crucible under a layer of the double chloride of aluminum and sodium, a pure button of aluminum is eventually obtained.

(564) As prepared by Deville's process, aluminum is a white malleable metal, nearly resembling silver in colour and hardness: it may be rolled into very thin foil and admits of being drawn into fine wire; after it has been rolled, it becomes much harder and more elastic. It conducts electricity nearly as well as silver. Aluminum

is remarkably sonorous, and emits a clear, musical sound when struck with a hard body. Fused aluminum crystallizes readily as it cools, apparently in regular octohedra; its point of fusion is below that of silver. It may be heated intensely in a current of air in a muffle without undergoing more than a superficial oxidation, and it is but slowly oxidized when heated to full redness in an atmosphere of steam.

Nitric acid is without action upon aluminum at the ordinary temperature, and dissolves it very slowly even when boiled upon the metal. Hydrochloric acid, on the contrary, whether concentrated or dilute, rapidly attacks it, forming chloride of aluminum, whilst hydrogen is disengaged. Solutions of the alkalies, especially when aided by heat, also dissolve aluminum, producing alumina which dissolves in the alkaline solution, whilst hydrogen gas is liberated. From its lightness and inalterability in the air, aluminum has been applied to the preparation of small weights, and a balance beam constructed of this metal was exhibited in the French Universal Exhibition for the year 1855.

Aluminum readily forms alloys with copper, silver, and iron, but it may be melted with lead without any combination between the two metals taking place. Its alloys with copper are white, very hard, and susceptible of a high polish. With carbon and silicon aluminum also combines readily, forming greyish, granular, brittle, and crystalline compounds, which present a considerable analogy to cast iron. It does not combine with mercury.

Finely divided aluminum burns brilliantly in the vapour of sulphur, and forms a black, semi-metallic sulphide ( $\text{Al}_2\text{S}_3$ ), which is rapidly decomposed by water, with formation of hydrate of alumina and sulphuretted hydrogen.

(565) *Oxide of Aluminum; Alumina*, ( $\text{Al}_2\text{O}_3$ ); *Eq.* 51.5; *Sp. Gr. of ruby* 3.95.—This is the only known oxide of aluminum; from its isomorphism with the sesquioxide of iron, and its general resemblance to it in properties, it is regarded as a sesquioxide. It forms one of the materials that enter most largely into the composition of the superficial strata of the earth. It is the basis of all the varieties of clay, and is present in greater or less quantity in almost every soil. It occurs nearly pure and crystallized in six-sided prisms, in *corundum*, in which mineral it has a specific gravity of 3.95, and is hard enough to cut glass. The *sapphire* and the *ruby* are also composed of this earth, tinged with a small quantity of oxide of iron. They are only inferior to the diamond in hardness. *Emery*, which from its hardness is so largely used

in grinding and polishing, is another form of alumina, coloured with oxides of iron and manganese.

To obtain alumina, it is sufficient to ignite pure ammonia alum ( $\text{NH}_4\text{O}, \text{SO}_3 + \text{Al}_2\text{O}_3, 3 \text{SO}_3 + 24 \text{aq}$ ) intensely for some time; the water, ammonia, and sulphuric acid escape, and anhydrous alumina is left. It is, however, nearly impossible to expel the last portions of sulphuric acid, as the salt swells up enormously and forms a white, porous, infusible mass, which is an extremely bad conductor of heat. Alumina may also be procured from alum quite free from iron, which should be dissolved in water and precipitated by carbonate of potash in slight excess: the liquid should be warmed, and the precipitate well washed: as traces of potash always adhere to it obstinately, it must be redissolved in hydrochloric acid, and then thrown down by ammonia or carbonate of ammonia: it falls as a white, semi-transparent, bulky, gelatinous hydrate, which must be again thoroughly washed. In this form alumina is completely soluble in potash, and is readily taken up by acids. On drying it contracts very much, and forms a yellowish, translucent mass, like gum. *Diaspore* is a natural hydrate ( $\text{Al}_2\text{O}_3 + \text{aq}$ ), which decrepitates strongly when heated, and falls to powder.

The hydrate of alumina when ignited loses its water, and at a certain temperature presents an appearance of sudden incandescence; it contracts greatly at the moment that this effect is produced, and is afterwards nearly insoluble in acids. Hydrate of alumina is strongly hygroscopic, and adheres to the tongue when applied to it.

Alumina fuses before the oxyhydrogen blowpipe, and yields a colourless, transparent mass, resembling corundum. It forms salts with the more powerful acids, but these salts are readily decomposed: they all have an acid reaction; and indeed alumina possesses properties which approach somewhat to those of an acid, for it has a strong tendency to unite with basic oxides. The *spinelle ruby*, for example, is a native aluminate of magnesia ( $\text{MgO}, \text{Al}_2\text{O}_3$ ), and *galinite* is an aluminate of zinc ( $\text{ZnO}, \text{Al}_2\text{O}_3$ ). Fremy has also obtained a white granular compound of alumina with potash, to which he assigns the formula ( $\text{KO}, \text{Al}_2\text{O}_3$ ). When the solution of alumina in potash is exposed to the air it absorbs carbonic acid, and a terhydrate of alumina is deposited in regular crystals.

Alumina when combined with silica forms clay, which is the basis of porcelain and of earthenware. To the dyer and the calico printer the compounds of alumina are of high value: the



hydrate of alumina has the property of combining intimately with certain kinds of organic matter, and when salts of alumina are mingled with coloured vegetable or animal solutions, and precipitated by the addition of an alkali, the alumina carries down the greater portion of the colouring matter, forming a species of pigment termed *lakes*. By soaking the cloth with a preparation of alumina, the earth attaches itself to the fibre; and if cloth thus prepared be plunged into a bath of the colouring matter, it becomes permanently dyed. Most colouring matters would be removed by washing, were it not for the intervention of some *mordant*, or substance which thus adheres to the fibre as well as to the colouring matter. Binoxide of tin and the sesquioxides of iron and chrome resemble alumina in this respect, and are largely used as mordants in dyeing calicoes and woollens.

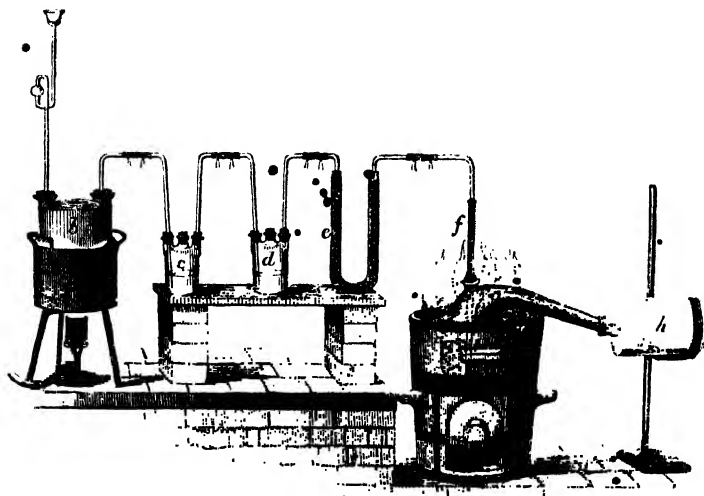
Mr. Crum (*Q. Journ. Chem. Soc.* vi. 216) has described a remarkable modification of hydrate of alumina, which, in the presence of a very small proportion of acetic acid, is largely soluble in water, and is coagulated and rendered insoluble by a minute trace of sulphuric acid. It appears probable from the experiments of Péan de St. Gilles (*Chem. Gaz.* 1855, p. 165) that sesquioxide of iron admits of a similar modification: these compounds will be further alluded to when the salts of acetic acid are described.

(566) *Chloride of Aluminum*, ( $\text{Al}_2\text{Cl}_3$ ); *Eq.* 63.—The anhydrous chloride of aluminum cannot be formed directly by dissolving alumina in hydrochloric acid and evaporating to dryness; since during the expulsion of the water a great part of the acid is also driven off. It may be procured as a yellow, anhydrous, volatile sublimate, by a process devised by Oersted:—alumina, mixed with charcoal powder, is made up into paste with starch or oil, and subdivided into pellets; these pellets are charred in a covered crucible, and then exposed to ignition in a current of dry chlorine. In this operation carbon, in a very finely divided state, is mixed with the alumina: when the mass is heated with chlorine the carbon unites with the oxygen of the alumina, and the chlorine seizes the liberated aluminum;  $\text{Al}_2\text{O}_3 + \text{C}_3 + \text{Cl}_3 = \text{Al}_2\text{Cl}_3 + 3 \text{CO}$ . The chloride of aluminum condenses in the cool part of the tube in a crystalline, somewhat translucent mass, or as an amorphous powder.

M. Deville prepares the chloride of aluminum in large quantity by means of an apparatus similar to that shown in fig. 301: *b* is a vessel containing a mixture of binoxide of manganese and hydrochloric acid, for generating chlorine; *a* is a water jacket, for apply-

ing a moderate heat; *c* is a wash-bottle containing water; *d* contains sulphuric acid; *e* is a bent tube filled with pumice stone soaked

FIG. 301.



with oil of vitriol, to remove the last traces of moisture; *g* is an earthen retort filled with the mixture of charcoal and alumina, heated by a charcoal fire. The chlorine is conveyed nearly to the bottom of this retort by means of a porcelain tube, *f*, luted into the tubulure: the gas reacts upon the mixture in the retort, forming carbonic oxide and chloride of aluminum; and the chloride of aluminum condenses in the gas-jar, *h*, which is placed for its reception: the open mouth of this jar is closed by means of a funnel, luted on with a strip of pasted paper; and the carbonic oxide escapes through the open tube, *i*, into the chimney. In order to purify the crude chloride of aluminum from the volatile perchloride of iron which usually accompanies it, the compound is redistilled from iron wire, by which the perchloride of iron is converted into protochloride, which is not volatile, and the chloride of aluminum sublimates in a state of purity.

If chloride of aluminum be heated in considerable mass, it melts at a dull red heat, and near its fusing point sublimates rapidly; when exposed to the air it emits fumes of hydrochloric acid; it is very deliquescent, and when thrown into water hisses from the heat developed by the violence of the combination. This solution, when concentrated by a very moderate heat, yields crystals which contain 12 equivalents of water (Bonsdorff). It is soluble in alcohol. By subliming chloride of aluminum in a current of sulphuretted

hydrogen it forms a combination with this gas : this compound is decomposed by resublimation, or by solution in water. It may also be made to combine with phosphuretted hydrogen and with ammonia.

*Fluoride of Aluminum* occurs native, combined with fluoride of sodium, forming *cryolite* ( $3 \text{ NaF} + \text{Al}_2\text{F}_3$ ). It has lately been obtained in large quantity from Greenland, and as it is easily decomposed by sodium it has been employed by Percy and by Rose as a source of metallic aluminium (*Phil. Mag.*, Oct. 1855).

Another highly prized aluminous mineral, containing fluorine, is the *topaz*, which is extremely hard ; the colourless variety of it has a lustre which has sometimes caused it to be mistaken for the diamond. Its composition is represented by the formula  $2 (\text{Al}_2\text{O}_3, \text{SiO}_2) + \text{Al}_2\text{O}_3, \text{SiF}_2$ .

(567) *Sesquisulphate of Alumina* ( $\text{Al}_2\text{O}_3, 3 \text{ SO}_3, 18 \text{ aq}$ ), *Eq.* 171.5 + 162.—This salt is formed by dissolving alumina in sulphuric acid. It is now manufactured on a large scale in the north of England, by acting upon clay with undiluted sulphuric acid, and is sold under the name of concentrated alum. It crystallizes in thin flexible scales which are soluble in twice their weight of cold water ; this solution may be used as a test for potash ; by mixing it with a solution containing a salt of this alkali, and by evaporating, octohedral crystals of alum are deposited.

(568) *Alum ; Sulphate of Alumina and Potash*, ( $\text{KO}, \text{SO}_3 + \text{Al}_2\text{O}_3, 3 \text{ SO}_3 + 24 \text{ aq}$ ) ; *Eq.* 258.5 + 216 ; *Sp. Gr. anhydrous*, 2.228, *Crystallized*, 1.726.—This important salt is occasionally found native in volcanic districts in the form of a white efflorescence, produced by the action of the sulphuric acid of the volcano upon the alumina and potash contained in the lava and trachytic rocks. For the purposes of commerce, however, alum is manufactured artificially. Three principal methods are adopted :—

1. The simplest is that practised in Italy, where, especially in the neighbourhood of Civita Vecchia, the alum rock or alum stone is abundant. This rock contains the elements of alum with an excess of hydrate of alumina, mixed with a variable proportion of siliceous matter. The ore is first roasted at a gentle heat in kilns, avoiding direct contact with the fuel : water is thus expelled, and the mass is rendered spongy ; the hydrate of alumina is decomposed, and the formation of a basic sulphate of alumina and potash, which is insoluble in water, is thereby prevented : the roasted ore is then arranged in long heaps or ridges upon a firm clay floor, where it is frequently moistened with water ; in the course of two or three months, the mass crumbles down into a sort of mud, which is lixiviated, and by evaporation

yields crystals of alum, which, after a second crystallization are fit for the market. This variety of alum crystallizes in opaque cubes, which retain subsulphate of alumina.

2. Alum may be procured, as in France, by gently igniting pipe-clay, or some other clay free from iron, then grinding it to fine powder and mixing it with half its weight of sulphuric acid; the mass is exposed to heat in a reverberatory furnace, stirring frequently till it becomes stiff; it is then removed, and exposed to the air for 4 or 5 weeks; the clay is gradually decomposed by the acid, and sulphate of alumina is formed; this salt is afterwards lixiviated out, and converted into alum by the addition of sulphate of potash.

3. A third process is resorted to in England and Germany for the purpose of turning alum schist to good account. This mineral is abundant at Whitby, in Yorkshire, and in the neighbourhood of Glasgow: it is a bituminous shale, found amongst the lower beds of the coal measures, and it contains a large quantity of very finely divided iron pyrites, disseminated through its mass which is composed chiefly of a siliceous clay. The mineral is decomposed either by exposure to the air or, as is more usually practised, by a slow roasting, conducted upon the ore arranged with alternate layers of fuel in long heaps or ridges, which are covered more or less completely with spent ore, in order to regulate the heat and to absorb the excess of sulphuric acid. In this operation the pyrites, or bisulphide of iron, is converted into the protosulphide of iron, losing half its sulphur, which absorbs oxygen and is converted into sulphuric acid; this acid unites with the alumina, while the protosulphide of iron, gradually combining with more oxygen, is converted into protosulphate of iron, or green vitriol;  $\text{FeS}_2 + \text{O}_3 = \text{FeS} + \text{SO}_3$ ; and  $2\text{FeS} + \text{O}_4 = \text{FeO} + \text{SO}_3$ . Great care is required to prevent the temperature from rising too high, a circumstance which would be attended with decomposition of the sulphate of alumina and loss of sulphuric acid. After the roasting is complete, the mass is greatly reduced in bulk, and is rendered porous and freely permeable to the air; the heap is allowed to lie exposed to the atmosphere, and is moistened from time to time; it is then lixiviated, and the protosulphate of iron is separated from the sulphate of alumina by crystallization of the liquor. The mother liquors often yield sulphate of magnesia when concentrated further.

In the Whitby alum works, in which the quantity of the sulphate of alumina much exceeds that of the sulphate of iron in solution, the concentration is completed in leaden pans; being carried so far

as that the liquid shall, when cold, be perfectly saturated, but shall deposit no crystals. The liquid is then run off into the precipitating tank, where it is mixed with a saturated solution of sulphate of potash, or, still better, of chloride of potassium, in quantity sufficient (as found by trial on the small scale) to yield the maximum proportion of alum. The mixture is briskly agitated, and the double sulphate of alumina and potash, which is sparingly soluble in cold water, is deposited in minute crystals, technically termed alum meal or flour. When chloride of potassium is used the sulphate of iron is decomposed, sulphate of potash is produced, and the very soluble protochloride of iron is retained in the liquor;  $KCl + FeO, SO_3 = KO, SO_3 + FeCl$ . To produce 100 parts of crystallized alum between 18 and 19 parts of sulphate of potash are required, or about 16 parts of the chloride of potassium. The mother-liquor is drained off and preserved, and the crystals, which have a reddish-brown colour from adhering iron, are twice washed by subsidence with a small quantity of cold water, being well drained after each washing. The crystals are then dissolved by heat in as small a quantity of water as possible, and the solution is run off into crystallizing barrels, which in ten days or a fortnight are taken to pieces; the crystalline mass is broken into fragments, drained, and sent into the market.

In the Scotch alum works at Campsie, in the neighbourhood of Glasgow, alum meal is not formed; but the hot liquor from the evaporating pan is run into a stone cooler, in which the necessary quantity of dry chloride of potassium has been placed. The liquid is thoroughly agitated and left to cool; on the sides of the vessel large crystals of alum form in four or five days; they are washed, and recrystallized twice.

Where sulphate of ammonia can be obtained sufficiently cheap, it may be substituted for sulphate of potash in the manufacture of alum; as the double salt which it forms with sulphate of alumina crystallizes with almost as much facility as the potash salt; it constitutes what is known as ammonia alum. Indeed, for the purposes to which alum is applied, neither the sulphate of potash nor that of ammonia is essential; the object proposed in the manufacture of alum being to obtain a salt of alumina which, by the facility with which it crystallizes, can be freed from iron and from earthy impurities.

A number of other salts may be procured which have the same crystalline form as potash alum and are similar to it in constitution; thus, sulphate of potash may be displaced by sulphate of soda, and

a soda alum may be formed, but the compound is much more soluble than potash alum: in like manner the place of the sesquisulphate of alumina may be supplied by sesquisulphate of iron, of chrome, or of manganese, forming a remarkable series of isomorphous compounds, some of which are enumerated in the annexed table:—

Potash alum	. . .	KO,	SO <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> ,	3 SO <sub>3</sub> + 24 aq
Ammonia alum	. . .	H <sub>4</sub> NO,	SO <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> ,	3 SO <sub>3</sub> + 24 aq
Soda alum	. . .	NaO,	SO <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> ,	3 SO <sub>3</sub> + 24 aq
Iron alum	. . .	KO,	SO <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> ,	3 SO <sub>3</sub> + 24 aq
Chrome alum	. . .	KO,	SO <sub>3</sub> + Cr <sub>2</sub> O <sub>3</sub> ,	3 SO <sub>3</sub> + 24 aq
Manganese alum	. . .	KO,	SO <sub>3</sub> + Mn <sub>2</sub> O <sub>3</sub> ,	3 SO <sub>3</sub> + 24 aq

Besides these true alums, a number of double salts of alumina may be formed with the sulphates of the oxides isomorphous with magnesia, which crystallize in fine silky needles. A native sulphate of alumina and manganese was found by Kane and by Apjohn to contain 25 equivalents of water, for which Graham proposes the formula, MnO, SO<sub>3</sub>, HO + Al<sub>2</sub>O<sub>3</sub>, 3 SO<sub>3</sub>, 24 aq, representing a compound of 1 equivalent of the sulphate of manganese with its equivalent of constitutional water, in combination with the tersulphate of alumina. A similar salt of iron has been met with in the native state.

Ordinary alum has a sweetish, styptic taste; it is soluble in about 18 parts of cold water, and in less than its own weight of boiling water. The solution has a strong acid reaction, and dissolves iron and zinc with evolution of hydrogen. When heated, this salt froths up, and loses its water of crystallization which amounts to nearly half its weight, forming, as it loses water, a tough tenacious paste, which is ultimately converted into a voluminous, white, infusible, porous mass of anhydrous or *burnt alum*. If crystallized alum be submitted to a regularly increasing heat, a certain proportion of the water contained in it is readily driven off: thus by a temperature of 212°, 10 equivalents out of the 24 are expelled, and 10 more at 248° F. If the salt be now heated to 392°, it is rendered anhydrous and insoluble in water (Gerhardt *Journ. de Pharm.* III. xii. 65). By ignition, alum loses a great part of its acid.

Alum is largely employed in dyeing. Its solution is gradually mixed with carbonate of soda, so long as the precipitate is redissolved on agitation, which happens till two-thirds of the acid have been neutralized. The salt employed, therefore, is a solution of Al<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub> + KO, SO<sub>3</sub> + 2(NaO SO<sub>3</sub>). Cloths dipped into this liquid remove the alumina thus redissolved, and contract an intimate, mechanical

combination with it, by which they are enabled, as already mentioned, to retain the colours of the dye stuffs employed. Upon evaporation, cubic crystals of alum are deposited from this solution, and the excess of alumina separates. A hydrated subsulphate of alumina,  $(\text{Al}_2\text{O}_3, \text{SO}_3 + 9 \text{ aq})$ , containing the same proportion of sulphuric acid and alumina as that formed in the mordanting liquid just described, is obtained by precipitating the sesquisulphate of alumina by caustic ammonia; it is a white insoluble powder. A white earthy-looking mineral, termed *aluminite*, said to have the same composition as this subsulphate, is found near Newhaven.

(569) *Phosphates of Alumina*.—Several minerals occur, into the composition of which phosphate of alumina enters. The blue *turquoise* is a hydrated native phosphate,  $2\{\text{Al}_2\text{O}_3, \text{PO}_5\} + 5 \text{ aq}$ , coloured by oxide of copper and oxide of iron. *Gibbsite*, which was formerly considered to be a hydrate of alumina, was found by Hermann to consist of a hydrated phosphate of the earth, mixed with variable proportions of hydrate of alumina. Phosphate of alumina,  $(\text{Al}_2\text{O}_3, \text{PO}_5)$ , may be prepared artificially by mixing solution of phosphate of soda with solution of alum; the precipitate must be well washed. If this precipitate be redissolved in an acid, and ammonia be added, the precipitate thus occasioned, has, according to Rammelsberg, the composition  $(4 \text{ Al}_2\text{O}_3, 3 \text{ PO}_5, 18 \text{ aq})$ . *Wavellite* is a mineral which crystallizes in tufts of radiated needles; according to Berzelius, it is a combination of fluoride of aluminium with the last mentioned subphosphate of alumina,  $3(4 \text{ Al}_2\text{O}_3, 3 \text{ PO}_5 + 18 \text{ aq}) + \text{Al}_2\text{F}_3$ . The mineral, *amblygonite*, is a combination of the same subphosphate of alumina with phosphate of lithia,  $(2 \text{ LiO}, \text{PO}_5 + 4 \text{ Al}_2\text{O}_3, 3 \text{ PO}_5)$ . *Lazulite* is a blue mineral composed of another double phosphate which contains the same phosphate of alumina,  $2(3 [\text{CaMgFe}] \text{O}, \text{PO}_5) + (4 \text{ Al}_2\text{O}_3, 3 \text{ PO}_5) + 6 \text{ aq}$ , coloured by subphosphate of iron (Rammelsberg).

Phosphate of alumina, in its hydrated form, is readily soluble in hydrochloric acid. Its solution may be precipitated by potash, but the precipitate is redissolved by an excess of the alkali. In the operations of analysis it is often necessary to separate phosphoric acid from alumina: this is most readily effected by Otto's method, in which the hydrochloric solution is mixed with tartaric acid, and then with ammonia and chloride of magnesium; the phosphoric acid precipitates as the double phosphate of magnesia and ammonia,  $(\text{H}_4\text{NO}, 2 \text{ MgO}, \text{PO}_5 + 12 \text{ aq})$ , and the whole of the alumina remains in solution.

(570) *SILICATES OF ALUMINA*.—The compounds of silica with alumina are numerous and important. All the varieties of clay

consist of hydrated silicate of alumina more or less mixed with other matters derived from the rocks which, by their disintegration, have formed the clay. Clay is, in fact, the result of the combined action of air and water upon felspathic and siliceous rocks, and therefore necessarily varies considerably in composition. The fundamental constituent of the more important varieties of clay, according to the researches of Brongniart, of Malaguti, and others, is represented by the formula,  $\frac{1}{2} \text{Al}_2\text{O}_3, \frac{2}{3} \text{SiO}_2 + \frac{1}{3} \text{aq}$ . This appears to be the composition of the fire clay of the Staffordshire coal measures. The ordinary varieties of clay, however, contain fragments of undecomposed rock, a certain proportion of potash, and variable amounts of silica in the hydrated condition, mixed with oxide of iron, lime, and magnesia; the character of the clay is materially modified according as one or other of these ingredients predominates.

Pure clay, before it has been ignited, forms, when kneaded, a tenacious, plastic paste, which is insoluble in water, but may readily be diffused through it in particles which are in an extreme state of subdivision; the deposit, when freed from the excess of water, as it subsides, resumes its plastic character. This paste, when slowly dried, and exposed to a high temperature, shrinks very much, and splits into masses which are extremely hard, but they do not undergo fusion in the furnace. Pure hydrated silicate of alumina is very slowly acted upon by hydrochloric or by nitric acid; but it is decomposed when heated with concentrated sulphuric acid; and upon this fact one of the processes for preparing alum (568) is founded. A gentle roasting of the clay, previous to the addition of the acid, frequently favours its disintegration; but ignition at a high temperature renders it proof against the action of all acids. Strong solution of potash dissolves unburnt clay very slowly; but if alkali in excess be fused with clay, the resulting mass is rendered easily soluble in water.

The intermixture of lime, magnesia, or oxide of iron, in any considerable quantity with the clay, greatly increases its fusibility, diminishes its plasticity, and causes it to be more readily attacked by acids; whilst an excess of silica renders it less fusible.

Clay emits a peculiar argillaceous odour when breathed upon or slightly moistened: its presence in any soil may be roughly but readily distinguished by the absorbent quality which it exhibits when applied in a dry state to the tongue or the lips; it adheres to them strongly, and absorbs the saliva from their surface. This absorbent property of clay causes it to retain ammonia in the soil to an extent which is of great importance to growing plants, and,



as Mr. Way has shown, it arrests the ammoniacal portions of the manure applied to the surface, and thus not only ministers to the growth of the crop, but exerts a very important purifying influence upon water impregnated with organic and other substances, which find their way slowly through the soil. Indeed, he has shown that mere agitation of such water with finely divided clay is sufficient to remove a considerable amount of the organic and saline matter previously in solution. Mr. Way found that both sulphate of ammonia and chloride of ammonium were partially decomposed by the lime of the clay, the ammonia being retained, whilst a corresponding amount of sulphate of lime or of chloride of calcium was formed in the solution. A similar decomposing action was also exerted upon nitrate of potash.

(571) The more important varieties of clay are the following :—

1. The celebrated *kaolin*, or porcelain clay of China, is a very pure white clay, which results from the decomposition of a granitic rock, the constituents of which are quartz, felspar, and mica, the felspar having gradually mouldered into this substance. A very similar description of clay is obtained near St. Austle, in Cornwall, and at St. Yrieix, near Limoges, in France. It is in these cases chiefly produced by the disintegration of a rock, known to geologists as *pegmatite*, which is, in fact, a species of granite in which mica is almost wanting, and quartz present in but small quantity. The *Cornish stone* used by the porcelain makers is the same rock in a less advanced stage of disintegration. The plasticity of kaolin is much less than that of the clay derived from disintegration of the secondary rocks.

2. *Pipeclay* is a white variety of clay, which is nearly free from iron. That of the Isle of Purbeck, in Dorsetshire, where it occurs nearly at the base of the clay deposits, is preferred; it is used in the manufacture of tobacco pipes without any addition; before the oxyhydrogen blowpipe it melts to a transparent, nearly colourless glass.

3. The *blue clay* of Devonshire and Dorsetshire is highly prized, as it is eminently plastic, and yields a white paste when fired. It is employed as one of the materials in the manufacture of porcelain.

The upper beds of clay frequently contain a large proportion of sand mixed with the plastic material, and are well suited for making salt-glazed stoneware without further admixture.

4. When the proportion of carbonate of lime in a clay is considerable, it constitutes what is known as a *marl*; if the aluminous

constituent preponderate, it forms an aluminous marl; if the carbonate of lime be in excess, it is a calcareous marl. The aluminous marls are extensively used in the manufacture of the coarser and more porous kinds of pottery.

5. *Loam* is a still more mixed substance, belonging to the more recent alluvial formations; it is the common material of which bricks are made; its red or brown colour is derived from the large proportion of peroxide of iron which it contains.

6. *Yellow ochre* and *red bole* are clays which derive their colour from oxide of iron, which is present in them in large quantity.

*Halloysite* is a white hydrated silicate of alumina which greatly resembles kaolin in appearance, but it is destitute of any plastic character, and is therefore unfitted for the manufacture of porcelain.

*Fuller's earth* is a porous silicate of alumina which has a strong adhesion to oily matters: if made into a paste with water, and allowed to dry upon a spot of grease upon a board or a cloth, it removes most of the oil by capillary action. Amongst other localities in England it is found abundantly near Reigate, in Surrey.

Besides these amorphous silicates of alumina, there are many which occur in a crystalline form. *Disthene*, or *cyanite*, is a blue-coloured soft mineral of this kind ( $\text{Al}_2\text{O}_3, \text{SiO}_2$ ).

The following table exhibits the composition of some of the more important varieties of clay used in the arts. The first two are results obtained by Ebelmen and Salvétat, the others are from analyses executed in Richardson's laboratory, and are quoted in the second volume of the English translation of Knapp's *Technological Chemistry* :—

	Washed kaolin.			Stour- bridge fire clay.	Pipe- clay.	Sandy clay.	Blue clay.	Brick clay.
	Chinese.	St. Yrieux.	Cornish.					
Silica . . .	50.5	48.37	46.32	64.10	53.66	66.68	45.38	49.44
Alumina . .	33.7	34.95	32.74	23.15	32.60	26.68	38.04	34.26
Oxide of iron	1.8	1.26	0.27	1.85	1.35	1.26	1.04	7.74
Lime . . .			0.36		0.40	0.84	1.20	1.48
Magnesia . .	0.8	trace	0.44	0.95	trace	trace	trace	5.14
Potash and soda }	1.9	2.40	12.67	10.00	12.04	5.14	13.57	1.94
Water . . .	11.2	12.62						
	99.9	99.40	99.80	100.05	99.49	100.00	100.23	100.00

(571 bis.) The *zeolites* are hydrated double silicates in which the principal bases are alumina and lime. They boil up when heated upon charcoal before the blowpipe, and dissolve in acids, leaving

the silica in a gelatinous state. In these minerals the lime is liable to displacement more or less complete by protoxide of iron, by magnesia, or by the alkaline bases. They are often very beautifully crystallized. *Analcime*, ( $\text{NaO}, \text{SiO}_2 + \text{Al}_2\text{O}_3, 3 \text{SiO}_2 + 2 \text{aq.}$ ) is one of these minerals; it crystallizes in cubes. *Stilbite* crystallizes in radiated needles, and has the composition of hydrated labradorite, ( $\text{CaO}, 3 \text{SiO}_2 + \text{Al}_2\text{O}_3, 3 \text{SiO}_2 + 6 \text{aq.}$ ) *Prehnite* crystallizes in six-sided prisms; it may be represented by the formula  $2 (\text{CaO}, \text{SiO}_2) + \text{Al}_2\text{O}_3, \text{SiO}_2 + \text{aq.}$

The varieties of *felspar*, ( $\text{MO}, 3 \text{SiO}_2 + \text{Al}_2\text{O}_3, 3 \text{SiO}_2$ ), are likewise double silicates of alumina with potash, soda, lithia, or lime. Potash felspar, the *adularia* or *orthoclase* of mineralogists, and the *petuntze* of the Chinese potters, is sufficiently hard to scratch glass; it is used as a glaze in the manufacture of the finest kinds of porcelain. Felspar requires the most intense heat of the porcelain furnace for its fusion, when it forms a white milky glass. Soda felspar, from its usual white colour, has received the name of *albite*. The felspar containing lithia constitutes *petalite*. Common, or potash felspar, crystallizes in oblique rhombic prisms. *Labradorite* is a double silicate of alumina, analogous to felspar, but it contains lime instead of the alkaline bases: it crystallizes in doubly oblique prisms belonging to the sixth system.

These minerals, by disintegration, yield the porcelain clay, or kaolin.

Felspar not only forms the regularly crystallized minerals just mentioned, but it occurs mingled with quartz and other crystallized minerals: it is indeed one of the most abundant constituents of many of the older rocks. *Granite*, for example, is a rock consisting of intermixed crystals of quartz, felspar, and mica. When it contains hornblende instead of mica, the term *syenite* is given to it. *Gneiss* contains the same components as granite, but it has a more stratified appearance, as the mica occurs more in layers. *Porphyry* consists chiefly of compact felspar, with crystals of felspar disseminated through it; it is often red or green, and takes a fine polish. *Basalt* is a dark-coloured volcanic rock, consisting of compact felspar containing crystals of augite. When the felspathic constituent is replaced by labradorite (or lime felspar), the basalt is called *dolerite*. *Trap*, or *greenstone*, is a very tough, compact, igneous rock, of a dark greenish or brownish-black colour; it is composed of an intimate mixture of felspar and hornblende. If it contain soda felspar (albite), the rock is known under the name of *diorite*. *Trachyte* is a volcanic rock also consisting chiefly of felspar,

less compact than either porphyry or basalt. The porous pumice-stone of volcanic districts is probably altered felspar; it contains a much smaller proportion of alkali than the crystallized mineral. Melted pumice constitutes *obsidian*, or volcanic glass.

*Garnet*, which commonly crystallizes in rhombic dodecahedra, and *idocrase*, which crystallizes in square prisms, are basic double silicates of lime and alumina, in which part of the lime is displaced by other protoxides, and the alumina by sesquioxide of iron,  $3(\text{Ca Mg Fe Mn}) \text{O} \cdot 2 \text{SiO}_2 + (\text{AlFe})_2\text{O}_3$ ,  $\text{SiO}_2$ . In *pyrope*, which is a species of garnet found in Bohemia, the colouring matter is partly sesquioxide of chromium. These minerals have a hardness greater than that of quartz.

The different forms of mica are also double silicates of alumina, which contain in addition a small quantity of water and of some alkaline fluoride. *Uniaxal mica* consists chiefly of silicate of magnesia and silicate of alumina,  $2 [2 (\text{MgKFe}) \text{O}, \text{SiO}_2] + (\text{AlFe})_2\text{O}_3$ ,  $2 \text{SiO}_2$ . In biaxal mica,  $(\text{K Fe}) \text{O}, 3 \text{SiO}_2 + 3 [(\text{AlFe})_2\text{O}_3, \text{SiO}_2]$ , on the other hand, silicate of potash predominates. *Lepidolite* is a variety of biaxal mica in which silicate of lithia takes the place of silicate of potash.

Another important double silicate of alumina and magnesia constitutes *chlorite*,  $4(\text{Mg Fe}) \text{O}, \text{SiO}_2 + (\text{Al Fe}_2) \text{O}_3, \text{SiO}_2 + 3 \text{aq}$ , which occurs both massive and in crystals with a granular fracture, and is of a green colour. In the massive form of chlorite slate it occurs as one of the primitive rocks which is widely distributed. *Roofing slate* is an argillaceous rock which splits readily into thin laminae. There are many varieties of slate. *Mica slate*, as its name implies, contains particles of mica, to which it owes its glistening appearance. *Hornblende slate* contains hornblende in place of mica, and has little lustre.

(572) *Porcelain and Pottery Ware*.—In the preparation of earthenware the material employed is required to possess a plasticity equal to that of red-hot glass, and yet to be capable of being rendered by heat sufficiently firm and hard to resist the mechanical violence necessarily inflicted on it by daily use.

The basis of earthenware, porcelain and china, is silicate of alumina; it possesses the plasticity required, and when heated assumes a great degree of hardness. Pure silicate of alumina, however, contracts greatly and unequally on drying: the utensils made from it would consequently be liable to crack during their desiccation; in order, therefore, to diminish the amount of this

contraction, an addition of some indifferent powder, such as ground flint, is made; while to compensate for the loss of tenacity thus occasioned, and which is particularly experienced in the use of the fine clays employed for porcelain, some fusible material is added, which, at the temperature required for firing, undergoes vitrification and greatly assists in binding the mass together. According to the greater or less proportion of these fusible materials, the ware is more or less semi-transparent, and more or less subject, like glass, to fly on the application of sudden changes of temperature.

The articles which have passed through the kiln, and have thus acquired firmness, are rough and uneven, and the coarser kinds of ware are very porous.

It is usual, in order to give smoothness and uniformity to the surface, as well as to render the body of the ware impermeable to moisture, to cover it with a kind of flux or glaze, which melts at a lower temperature than the material composing the ware itself; and in order to melt the glaze the articles are a second time passed through the kiln.

The materials employed in the fabrication of porcelain and earthenware are clays of various degrees of purity and fineness, ground felspar, calcined flints or sand, burnt bones, chalk, and carbonate of soda or potash; they do not, therefore, very greatly differ from those which are employed in glass-making, except in the great preponderance of silicate of alumina. The varieties of pottery or earthenware are numerous: the following include those which are of most importance:—

1. *Porcelain, or China.*—This is the finest and most valuable description of ware: it is distinguished from ordinary earthenware by the composition of the paste from which it is formed. The materials are selected with great care, in order that they may give a colourless mass after firing. Porcelain consists mainly of two classes of materials, one of which, the clay, is plastic, and is infusible at the temperature employed to fire it; the other (chiefly silicate of lime and potash) softens and becomes vitrified, forming a kind of cement which binds the clay firmly together, and thus produces a translucent mass, which when broken appears of a uniform texture throughout, and is impervious to liquids. Much judgment is required in the due proportioning of the fusible and infusible materials.

The celebrated Sèvres porcelain resembles the original Chinese ware, of which, indeed, it is an imitation. Regnault states the composition of the paste used at Sèvres for ornamental purposes

to be the following:—Washed kaolin, 62 parts; Bougival chalk, 4; Aumont sand, 17; quartzose felspar, 17. As however the composition of the kaolin varies, the admixture of the other materials is necessarily varied also, so as to obtain a porcelain of uniform composition.

In order to give a smooth surface to the ware, a glaze similar in composition to the fusible material is used. The glaze employed at Sèvres consists of a mixture of felspar and quartz. It is transparent, and rather more fusible than the body of the ware, but becomes thoroughly incorporated with it, and from its similarity in composition it expands and contracts by heat uniformly with the paste which it covers; hence it is not liable to crack and split in all directions in the manner which is so commonly observed in the glaze of the more ordinary kinds of earthenware.

The china of Berlin and Meissen is very similar in composition to that of Sèvres: these constitute what is termed hard, or true, porcelain.

English porcelain contains, in addition to the Cornish clay and felspar or flint, a large proportion of burnt bones; the glaze, which is transparent, usually contains both borax and oxide of lead to increase its fusibility. English porcelain is softer than the Chinese, French, or German porcelain, and constitutes one variety of what the French term *porcelain tendre*, the manufacture of which in France is now rarely practised.

2. *Stoneware* is a species of porcelain in which the body of the ware is more or less coloured, less care being taken with regard to the purity of the material. It generally contains more oxide of iron, and consequently is somewhat more fusible than the best porcelain, and is usually salt-glazed in a manner shortly to be described. *Wedgwood-ware* is a fine description of stoneware.

3. *Fine Earthenware*.—Articles of this description are very extensively manufactured in the Staffordshire Potteries, and constitute the ordinary table service of this country. The Devonshire and Dorsetshire clays are those chiefly made use of; they are mixed with a large proportion of ground flints, and yield an infusible paste which burns nearly white. The body of the ware is not fused in the firing, but it is rendered impervious to liquids by means of a fusible lead glaze.

4. *Common Earthenware* is made of an inferior and more fusible description of clay: both this kind of ware and the foregoing one crack easily on the sudden application of heat.

5. The coarsest description of clay goods are bricks, tiles flowerpots, and similar articles.

6. Articles which are required to stand a high temperature, such as fire-bricks for lining furnaces, muffles, pots for the fusion of glass, crucibles for melting steel, and the Hessian crucibles so largely in demand in the laboratory, are made of a pure, infusible siliceous clay, the shrinking of which during drying is diminished by the addition either of burnt clay of the same description, or of what amounts to the same thing, broken pots of the same material, which are reduced to a fine powder and incorporated with the paste.

The following table gives the composition of some of the more important varieties of china and pottery ware :—

	Porcelain.					Wedg-wood ware.	Lambeth stone ware.	Hessian crucible.
	China.	Berlin.	English.	Sèvres.	Meissen.			
	C. Cowper.	Wilson.	Cowper.	Laurent.	Laurent.	Salvetat.	Salvetat.	Berthier.
Silica . . . . .	71'04	71'34	40'60	58'0	57'7	66'49	74'00	71
Alumina . . . . .		23'76	24'15	34'5	36'0	26'00	22'04	25
Oxide of iron . . . . .	22'46							
Lime . . . . .	3'82	1'74	14'22	4'5	0'8	6'12	2'00	4
Alkali . . . . .	2'68	0'57	5'28	3'0	0'3	1'04	0'60	
Magnesia . . . . .		0'20	0'43		5'2	0'20	1'06	
Bone earth and oxide of iron . . . . .			15'32		trace	0'15	0'17	
100'00	99'61	100'00	100'0	100'0	100'0	100'00	99'87	100'0

(573) For the finer kinds of porcelain much care is taken to ensure the purity and minute subdivision of the constituents, as well as their intimate admixture. The clay is first ground between horizontal stones under water; it is next levigated in water, to allow the coarser particles to subside while the lighter ones remain in suspension. The finer suspended particles are then formed into a mixture of the consistence of thin cream; a wine pint of this being made to weigh 24 or 26 ounces: in this state the cream or pulp is mixed with the ground felspar, flint, or other material. Suppose, for example, that the pulp is to be mixed with ground flints; the flints are heated to redness, suddenly quenched in cold water, and then reduced by stamping and grinding them under water to an impalpable powder; this also is suspended in water, a wine pint of the mixture being made to weigh 32 ounces. The two ingredients are easily mixed in the necessary proportions by taking a given measure of each pulp and thoroughly incorporating them. The mixture thus obtained is technically termed *slip*. The slip is well agitated and

allowed to subside ; the deposit is drained (carefully mixing it from time to time), and dried, until it has acquired sufficient consistence to allow of its being wrought by the potter. Much labour is afterwards bestowed in working this clay in such a manner as to render it of uniform composition throughout, and to preserve it free from air bubbles. It is generally considered that the mixture is greatly improved in quality by being allowed to remain some months before it is worked up, the mass being occasionally turned over and beaten.

Less labour is expended upon the coarser kinds of pottery. After the raw clay, brought from Devonshire or Dorsetshire in blocks of about 30 pounds weight, has been dried, it is ground and mixed with a certain proportion of ground flints ; it is then tempered with water into a stiff paste, and passed between rollers to complete the process of fitting it for the wheel.

The mechanical operations are of the same nature in every case ; and for fashioning the clay the *potter's wheel* is in general use. This consists of a circular slab which can be made to revolve in a horizontal plane, either by a treadle worked by the foot, or by a winch turned by a boy or girl. A mass of clay of the size required is dashed upon the moistened slab, and is worked by the hands, the wheel revolving during the whole time, so that the operation is a compound of moulding and turning ; the article is finally trimmed up with a wooden tool, and the work is detached from the wheel by passing a wire between the slab and the vessel. The moulded articles are then allowed to dry for a day or two in a room heated from 90° to 100° F., in order to give them firmness, to permit them, when necessary, to be carefully turned on a lathe. After this operation has been completed, the handles and ornaments may be attached ; these are made in moulds, and adhere readily by means of slip when pressed against the moulded mass, which is still moist. The articles have at this stage received the form which they are intended to retain, and are next subjected to heat in the *biscuit* furnace. It is necessary that the temperature be at first very gradually and carefully raised, lest the aqueous vapour, being extricated too suddenly, should deface the vessel or injure its texture. By this first firing the different articles acquire a greater degree of firmness, and can be handled without danger of breakage, but they are in a very porous state, technically termed *biscuit*. The ware in this stage readily absorbs any solution that may be placed upon its surface, and this is the period chosen for printing the patterns or designs which the finished goods are to exhibit. The colouring matter generally consists of some metallic oxide

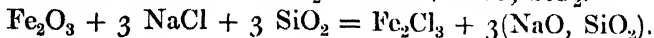
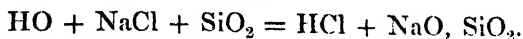


ground up with boiled linseed oil. Blue is usually given by oxide of cobalt; green by oxide of chrome; brown by a mixture of oxides of iron and manganese; black, by the black oxide of uranium; and a pink, which is much esteemed, by a combination of oxide of tin, lime, and a minute quantity of oxide of chrome. In order to apply the colouring material, it is printed from copper plates on a thin unsized paper made for the purpose; this paper, while the colour is still moist, is applied to the surface of the biscuit; the design is soon absorbed by the ware, and the paper is washed off. The ware is now subjected to another baking or firing, for the purpose of fixing the colour and burning off the oil. In the finer kinds of decoration, the application of the colouring matter requires the nicest management; for details upon this point, and indeed upon most others connected with the art of Pottery, the reader is referred to Brongniart's great work, *Sur les Arts Céramiques*. After the application of the colouring material the ware still remains far too porous for use, and it further undergoes the process of glazing.

The glaze of ordinary earthenware usually consists of a fusible material containing a considerable quantity of oxide of lead; a mixture of felspar, flint, flint glass, and white lead is in common use: it is ground into a thin paste with water, the articles are dipped in singly, and quickly absorb moisture, leaving the glaze on the surface, which when heated fuses and fills the pores.

The glazing of stone ware depends upon a peculiar mode of decomposition of common salt. Chloride of sodium is not decomposed by heat alone, and if heated with dry silicic acid no decomposition occurs; but in the presence of silica and some substance capable of imparting oxygen to the sodium, and at the same time of removing the chlorine with which it is united—such, for instance, as steam, or oxide of iron—the salt is susceptible of decomposition at an elevated temperature; silicate of soda and hydrochloric acid, or silicate of soda and perchloride of iron, as the case may be, being formed. The various utensils, having been dipped into sand and water, are placed in the kiln, and are gradually raised to an intense heat. A certain quantity of moist salt is then thrown in: the chloride of sodium is quickly converted into vapour, and the salt is decomposed by the silica, and the oxide of iron in the clay, aided by the steam produced in the combustion of the fuel in the furnace. The chloride of iron and hydrochloric acid pass off in vapour with the excess of salt employed, whilst the silicate of

soda fuses upon the ware, and renders it impervious to liquids. The reactions may be thus represented :—



It is worthy of remark that although clay contracts very evenly by heat, when its density is uniform throughout, yet if its density be unequal in different parts the contraction is also unequal; hence though a vessel may issue smooth and well finished from the workman's hands, it often assumes a striated and uneven appearance during the process of firing; and if a stamp be impressed upon clay while soft and the whole surface be shaved away until no further impression is visible, the mark of the stamp, after baking, reappears in a manner more or less distinct.

(574) *Ultramarine*.—Alumina enters into the formation of the pigment ultramarine, so highly prized for the purity and delicacy of its blue colour. This valuable colouring material was formerly obtained exclusively from the lapis lazuli by a tedious process, which consisted in gently calcining the stone, broken into fragments of the size of nuts; the heated fragments were then quenched in vinegar, by which they were rendered more friable, and were deprived of adhering carbonate of lime: they were next subjected to a patient levigation with a thin syrup of honey and dragon's blood; were then made into a paste with a resinous cement; and after allowing this to remain undisturbed for some days, the ultramarine was extracted from it by suspension in hot water and subsidence. Ultramarine is now, however, manufactured artificially upon a large scale. The following, according to M. Debette, are the more important steps of the process:—Fine clay is washed, in order to free it from sand, and the portions suspended in water are allowed to deposit. A crude sulphide of sodium is prepared by heating, in a reverberatory furnace, a mixture consisting of 3 parts of calcined sulphate of soda, 3 of lime slaked by exposure to the air, and 1 of powdered charcoal. The sulphide of sodium thus obtained is dissolved in water, and the excess of charcoal is allowed to subside; the clear liquor is decanted, (taking the greatest care not to carry over any particles of charcoal,) and is boiled with powdered sulphur, so as to form a pentasulphide of sodium. The liquid is next evaporated down to a syrupy consistence in iron pans: 50 parts of this sulphide are mixed with 12 of clay and 0.15 of protosulphate of iron free from copper; the sulphate is

immediately converted into sulphide of iron, and the mass becomes green. The mixture is then introduced into muffles and roasted for several hours at a carefully regulated heat, until it assumes a dark blue colour; before it reaches this point, it passes successively through various shades of brown, red, green, and ultimately becomes blue. The soluble salts are then removed from the roasted mass by washing; the residue is dried, and submitted to a second roasting at a low temperature, during which operation it is continually stirred; and at length it assumes the desired brilliant blue colour.

Ultramarine consists of silicate of alumina coloured probably by sulphide of sodium, since, according to Brunner, a corresponding compound, in which sulphide of potassium is substituted for sulphide of sodium, is colourless. The following is the composition of a specimen of ultramarine from lapis lazuli, according to the analysis of Varrentrapp, as contrasted with that of an artificial specimen by the same analyst (Poggendorff, *Annal.* xlix. 520):—

	Natural.	Artificial.
Silica . . . . .	45.50	45.604
Alumina . . . . .	31.76	23.304
Soda . . . . .	9.09	21.476
Sulphur . . . . .	0.95	1.685
Lime . . . . .	3.52	0.021
Sulphuric acid . . . . .	5.89	3.830
Iron . . . . .	0.86	1.063
Chlorine . . . . .	0.42	trace
Water . . . . .	0.12	KO, 1.752
	<hr/> 98.11	<hr/> 98.735

Ultramarine, if heated in the air, gradually assumes a dull green hue; when heated with sulphur, it is not changed; if melted with borax, sulphur and carbonic acid escape, and a colourless glass remains. Sulphuric, nitric, and hydrochloric acids decompose it; the colour is quickly destroyed, and all its constituents except silica are dissolved. Chlorine acts still more rapidly, dissolving everything but the silica, and completely discharging the colour.

(575) CHARACTERS OF THE COMPOUNDS OF ALUMINA. — The salts of alumina, with the exception of the chloride, are colourless. They have a sweetish, strongly astringent taste.

*Before the blowpipe* the compounds of aluminum are distinguished by the formation of a pale azure blue if moistened with nitrate of cobalt and gently ignited.

In solution, they give with *hydrosulphate of ammonia* a white

precipitate of hydrate of alumina, with evolution of sulphuretted hydrogen. *Ammonia* produces a bulky, semi-transparent, gelatinous precipitate of hydrate of alumina; it is insoluble in excess of ammonia, or its carbonate. *Potash* dissolves it readily; and it reprecipitates on adding muriate of ammonia in excess. The *carbonates of the alkalies* produce the same precipitate under disengagement of carbonic acid gas, but, according to Muspratt, it retains a portion of carbonic acid. *Sulphate of potash* and sulphuric acid in slight excess added to solutions of the salts of alumina, and evaporated, furnish well marked octohedral crystals of alum.

The quantity of alumina in the course of an analysis is always estimated from the precipitate by ammonia, or its carbonate or hydrosulphate; when thoroughly washed (an operation which from its gelatinous nature is tedious), and then ignited, it consists of the pure earth only.

(576) *Separation of Alumina from the Alkalies and Alkaline Earths*.—Supposing magnesia to be present in the liquid, solution of chloride of ammonium is first added to it unless it be powerfully acid; on the addition of caustic ammonia in slight excess, pure hydrate of alumina precipitates. Hydrosulphate of ammonia is a still better precipitant, if the liquid have been first nearly neutralized by ammonia; the precipitate is extremely voluminous, and requires persevering washing. On ignition it yields pure alumina. The alkalies and alkaline earths remain in the solution which has been filtered from the alumina, and their amount may be determined by the methods already detailed, (555, *et seq.*)

## § II. GLUCINUM.

*Symbol*, Gl; *Equivalent*, 6.97; *Specific Gravity*, 2.1.

(577) GLUCINUM is extracted from the emerald, or the beryl, which consist chiefly of silicate of alumina and glucina ( $\text{Gl}_2\text{O}_3, 3\text{SiO}_2 + \text{Al}_2\text{O}_3, 3\text{SiO}_2$ ). The metal is procured from its chloride in the same way as aluminum.

Glucinum, according to the experiments of Debray (*Ann. de Chimie*, III. xlv. 5), is a white malleable metal, of sp. gr. 2.1, fusible below the melting point of silver. It does not burn in air, oxygen, or the vapour of sulphur, but it combines readily with chlorine and iodine, and also with silicon. The vapour of water is not decomposed by it, even when the metal is heated to full red-

ness and exposed to it. Glucinum is readily dissolved by dilute hydrochloric and sulphuric acids; dilute or concentrated nitric acid acts but feebly upon it. It is, however, readily dissolved by potash, but is not acted upon by ammonia. Glucinum forms but one oxide; there is some doubt whether this should be regarded as a protoxide, or as a sesquioxide. Berzelius adopted the latter view, but later researches seem to throw considerable doubt upon the correctness of this hypothesis.

(578) *Glucina* ( $\text{Gl}_2\text{O}_3$ ), *Eq.* 38, *Sp. Gr.* 2.796, is extracted from the beryl, of which it constitutes 13.6 per cent.: the mineral is reduced to a very fine powder, fused with carbonate of potash, treated with hydrochloric acid, evaporated to dryness, again moistened with acid and heated with water, which dissolves everything except the silica; the filtered liquid is mixed with an excess of a solution of ammonia, which occasions a voluminous precipitate containing both alumina and glucina; this precipitate is well washed, and the glucina is dissolved out from the alumina by digesting the mass in a solution of carbonate of ammonia. It is again filtered, and upon boiling the clear liquid, carbonate of glucina is deposited as a white powder, which, when ignited, leaves pure glucina. Freshly precipitated glucina forms with water a somewhat tenacious mass, but it does not harden like alumina when ignited. The fixed and carbonated alkalis dissolve it readily. The hydrate is a bulky, white, gelatinous mass, which absorbs carbonic acid from the air. The *chloride* ( $\text{Gl}_2\text{Cl}_3$ ), *eq.* 120.5, is prepared in the same way as the chloride of aluminium; it sublimes in white, brilliant, fusible needles, which are very deliquescent; ~~an acid~~ <sup>a hydrated</sup> chloride may be obtained in crystals. Glucina combines with sulphuric acid in several proportions: one of these sulphates ( $\text{Gl}_2\text{O}_3, 3 \text{ SO}_3, 12 \text{ aq}$ ) crystallizes in octohedra: the other sulphates are amorphous sub-salts. An *aluminate of glucina* occurs native in the gem *chrysoberyl*,  $\text{Gl}_2\text{O}_3, 3 \text{ Al}_2\text{O}_3$ .

(579) *Characters of the Salts of Glucina*.—The salts of glucina have a sweet taste, (whence the name glucina was derived, from  $\gamma\lambda\alpha\kappa\upsilon\varsigma$ , sweet,) with a slight astringency. They are colourless, and are distinguished from those of alumina by not yielding an alum with sulphate of potash; nor a blue when heated before the blow-pipe with nitrate of cobalt; and by giving with *carbonate of ammonia* a white precipitate of carbonate of glucina, easily soluble in excess of the alkaline salt. *Ferrocyanide of potassium* gives no precipitate: a white precipitate of hydrate of glucina is produced by *sulphide of potassium*, with extrication of sulphuretted hydrogen.

If a hot solution of *fluoride of potassium* in excess be added to a hot solution of a glucina salt, scales of a sparingly soluble double fluoride of glucinum and potassium are formed. Glucina is always estimated in the form of the anhydrous earth.

### § III. ZIRCONIUM.

*Symbol, Zr; Equivalent, 33.58.*

(580) ZIRCONIUM is the metallic base of an earth contained in the zircon and the hyacinth, which are silicates of the earth. The metal is procured by heating the fluoride of potassium and zirconium with potassium, and dissolving the residue when cold in dilute hydrochloric acid; the zirconium may be separated in a pulverulent form, washed with solution of chloride of ammonium, and then with alcohol; if water be used for the washing, the zirconium passes through the filter with it in suspension. As thus obtained it is in the form of a black powder, which does not conduct a feeble voltaic current; under the burnisher it assumes a feeble metallic lustre. It has not been fused: when heated in the air or oxygen it takes fire below redness and burns brilliantly, forming zirconia of snowy whiteness: dilute sulphuric and hydrochloric acids do not act on it. Hydrofluoric acid dissolves it with extrication of hydrogen; boiling water gradually oxidizes it: heated with sulphur in vacuo it forms a brown pulverulent *sulphide* which is not decomposed by sulphuric or hydrochloric acids, and is but slowly attacked by aqua regia.

(581) *Zirconia* ( $\text{Zr}_2\text{O}_3$ ); *Eg.* 91. — Zirconium forms but one oxide, which is commonly regarded as the sesquioxide. It is obtained by fusing very finely powdered zircon with hydrate of potash or soda, and saturating with hydrochloric acid. The excess of acid and moisture is expelled by evaporating nearly to dryness; on the addition of water chloride of zirconium dissolves, leaving the silica; the solution is decomposed by excess of ammonia. Hydrate of zirconia precipitates, and is washed and ignited. Upon applying heat, it glows brightly just before ignition, and becomes much denser. Zirconia forms a white infusible powder, of sp. gr. 4.3, which, after ignition, is insoluble in acids, with the exception of strong sulphuric acid. The hydrate is a gelatinous bulky white precipitate, very sparingly soluble in carbonate of ammonia. It is insoluble in the caustic alkalies. If the salts of zirconia be precipitated by an alkaline carbonate, the precipitate redissolves if

agitated with excess of the alkali; a bicarbonate takes up still more, and by boiling the solution a portion of the earth is deposited. If a solution of sulphate of potash be boiled with sulphate of zirconia, a characteristic decomposition occurs, and the subsulphate of zirconia falls, whilst bisulphate of potash remains dissolved. The *chloride of zirconium* crystallizes in needles. It is soluble in water and in alcohol; the crystals effloresce in the air, and lose water and hydrochloric acid, leaving an oxychloride, which is soluble. Zirconia is distinguished from alumina and glucina by its insolubility in the *caustic alkalies*. Its salts have a purely astringent taste; when boiled with the *sulphate of potash*, a sparingly soluble subsulphate of the earth is formed. *Tincture of galls* gives a yellow precipitate in their solutions; *ferrocyanide of potassium* none.

It appears possible from the experiments of Svanberg, that zirconia is not a pure earth, but that it is a mixture of three.

#### § IV. THORINUM, YTTRIUM, ERBIUM, TERBIUM.

(582) THORINUM (*Eq.* 39.5), is procured from the rare black mineral *thorite*, found in a syenitic rock, in Norway. This metal, like aluminum, is obtained from its chloride. It much resembles aluminum, but takes fire considerably below redness, and burns with great brilliancy; the resulting oxide shows no traces of fusion. *Thorina* is considered to be a protoxide, and is remarkable for its high sp. gr. (9.402.) It is insoluble in the caustic alkalies, but dissolves without difficulty in their carbonates. Its salts are astringent, and give a white precipitate with ferrocyanide of potassium. It forms with sulphate of potash a double sulphate of potash and thorina, which is soluble in water, but is precipitated by a saturated solution of sulphate of potash. The sulphate of thorina exhibits the characteristic peculiarity of being precipitated by boiling its solution, but it dissolves slowly on cooling. Its crystals, when heated, become milk white without altering in form, like those of sulphate of yttria. Oxalic acid gives with salts of thorina, even in acid solutions, a white insoluble oxalate of the earth.

(583) YTTRIUM is obtained by a method similar to that employed for aluminum and glucinum. This metal is not oxidized when heated to redness either in air or in aqueous vapour; in oxygen it burns with superb scintillations; dilute acids and alkalies slowly dissolve it.

*Yttria* is a very rare earth, found in *gadolinite*, which is a silicate of yttria, glucina, cerium, and iron; it occurs also in *ytthro-*

*tantalite* combined with columbium, and in one or two other very rare minerals. It is considered to be a protoxide, and forms a white earthy powder of sp. gr. 4.842; it is insoluble in the caustic alkalies, but the alkaline carbonates, especially that of ammonia, dissolve it.

Its salts have a sweetish astringent taste, and yield a white precipitate with ferrocyanide of potassium. Its most characteristic salt is the sulphate, which forms pink crystals, which lose water at  $104^{\circ}$ , and become milk white, without change of form; on being put into water they do not resume their transparency.

Mosander states that three bases have been confounded under the name of yttria; to the more abundant of these he gives the name of yttria; the other two he distinguishes as *erbia* and *terbia*. The oxide of erbium has a yellowish tint, but its salts are colourless; the salts of terbium have a pale rose colour.

#### § V. CERIUM, LANTANIUM, AND DIDYMIUM.

(584) Closely allied to the metals of the earths of which a brief mention has just been made, are three other metals, the oxides of which, being more or less coloured, have not generally been considered as belonging to the earths proper. They need no lengthened description, as they have hitherto been found only in a few rare minerals, of which cerite, a hydrated subsilicate of cerium, is the most common. Till recently they were all confounded together under the name cerium.

CERIUM appears to form two oxides—a protoxide, and a sesquioxide, both of which yield salts with acids. The best known of these is the double sulphate of protoxide of cerium and potash, which is insoluble in sulphate of potash. The sesquioxide has a yellowish tinge, and its salts are yellow or red.

LANTANIUM forms only one oxide, which is buff-coloured, and freely soluble in dilute nitric acid. It forms colourless astringent salts, which give a white precipitate with the soluble oxalates.

DIDYMIUM also furnishes but a single oxide, which is of a dark brown colour, when anhydrous; in the hydrated state it absorbs carbonic acid from the air. Its salts are pink or violet-coloured, and are not precipitated in the cold by sulphide of ammonium.



## CHAPTER XIV.

## GROUP IV.—METALS MORE OR LESS ALLIED TO IRON.

## § I. ZINC.

*Symbol, Zn; Equivalent, 32.52; Specific Gravity, 6.8 to 7.1.*

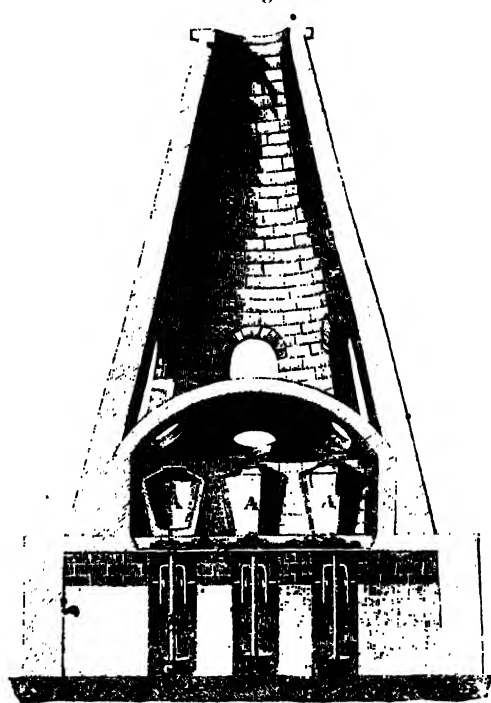
(585) ZINC, or *spelter*, as it is often called in commerce, is a metal, the ores of which occur in considerable abundance, though it is never met with in the native state. Much of the zinc of commerce is supplied from Sillesia, where the ore wrought is *calamine*; the common or rhomboidal calamine, a carbonate of zinc, is the most important variety, though the prismatic or electric calamine, a hydrated subsilicate of zinc, is found often in the Carinthian ores: it is much more difficult of reduction. Carbonate of zinc is also extensively worked in Belgium, where it is found mixed with clay. In the Mendip Hills, in Somersetshire, the carbonate of zinc is associated with magnesian limestone. *Blende*, or sulphide of zinc, is worked in England to some extent; it usually accompanies the sulphide of lead or galena in the mountain limestone. In New Jersey *red oxide of zinc* has been found in large quantities both massive and crystallized; the colour is due to admixture with oxides of manganese and iron. It forms a valuable ore, and is easily reduced.

(586) *Extraction of Zinc from its Ores.*—In the extraction of zinc, whether from blende or from calamine, the ore is crushed between rollers, and undergoes a process of roasting, which in the case of blende is tedious and requires to be carefully performed; the sulphur burns away as sulphurous acid, and the zinc becomes oxidized;  $\text{ZnS} + 3 \text{O} \text{ yield } \text{ZnO} + \text{SO}_2$ . Calamine also yields oxide of zinc when roasted, whilst the carbonic acid and water are expelled. The roasted ore from either source is mixed with half its weight of powdered coke or anthracite, and introduced into crucibles of peculiar construction. The method of reduction practised in England offers one of the few instances in which distillation, *per descensum*, is still practised:—a circular furnace, somewhat similar to that used in making glass, is employed: in

this furnace six large crucibles, (three of which are represented in the section at A A A, fig. 302,) each 4 feet high and  $2\frac{1}{2}$  feet in diameter, are arranged, three on each side of the firebars; one of these crucibles is shown in section in the figure. In the bottom of each crucible is an opening, to which a short iron pipe is attached, which passes out through the bottom of the furnace; to this iron tube a second wider tube, *b*, about eight feet long, is fastened in such a manner as to be readily removable; beneath the open end of this tube a sheet-iron vessel, *c*, is placed to receive the zinc. The bottom

of the crucible is then loosely plugged with large pieces of coke, and a charge containing from four to five hundred weight of the mixture of calcined ore and coal is introduced into each pot and the cover is carefully luted on. Carbonic oxide is first evolved abundantly, and burns with a blue flame at the mouth of the short iron tube; in a few hours the colour of the flame changes to white, and it begins to deposit white fumes of oxide of zinc. The flame is then extinguished by attaching

FIG. 302.



the longer tube, and the metal, which is condensed partly in powder, partly in stalactitic masses, falls down into the iron vessels, *c c*, placed for its reception. The zinc, being volatile at very high temperatures, boils and distils as the operation proceeds. In order to prevent the pipe, *b*, from becoming choked, it is occasionally removed, and the zinc detached from it. The crude metal is mingled with a good deal of oxide; it is therefore re-melted, skimmed, and cast into ingots; or (if intended for rolling) into sheets, and then laminated at a tempera-

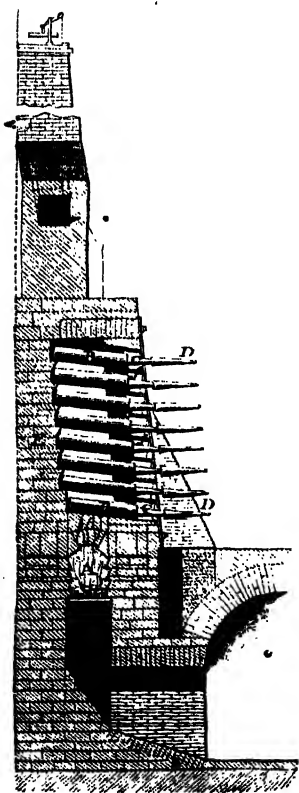
ture of about  $250^{\circ}$ . Calamine, which contains 60 per cent. of metal, does not yield on an average above 30; the greater part of the silicate of zinc, which calamine almost always contains, escaping decomposition.

(587) In Silesia the distillation is effected in muffle-shaped earthen retorts, which are ranged in two rows on the same plane in a long furnace, back to back: the outer end of each retort is provided with two apertures; the lower one is employed for introducing the charge, and is afterwards carefully luted up, whilst the upper one is for receiving a bent earthen pipe which carries off the metal as it distils.

(588) In Belgium the distillation is managed quite differently. The ores treated in that country are of two kinds, both occurring in a matrix of clay above a bed of dolomite; one is a red variety, containing about 33 per cent. of zinc, with a good deal of oxide of

iron, but admitting of reduction at a moderate temperature; the other is a white ore, also a calamine, which contains about 46 per cent. of zinc, and requires a much higher temperature for its reduction. These two species of ore are kept distinct from each other during the process of smelting. The calamine having been washed to remove the clay, is roasted, during which operation it loses about 25 per cent. of water and carbonic acid. After this it is reduced to a fine powder, and thoroughly mixed with half its weight of coal dust: this mixture is then introduced into clay retorts about three feet eight inches long and six inches in diameter; each retort is charged with about forty pounds of the mixture of coal and roasted ore. Forty-two of these retorts are arranged in an arched furnace, in rows of six, placed one above another. The backs of the retorts rest on notches in the wall, *e*, fig. 303, and are supported on a slightly higher level than the open extremities, which rest in front upon iron plates, *f, f, f*. To each re-

FIG. 303.



tort an open, somewhat conical, cast-iron pipe, c, is luted; this serves as a receiver for the distilled metal, and upon each of these receivers is fitted a second receiver of sheet-iron, d, with an opening at the extremity for the escape of gas. The fire by which the retorts are heated is shown at a. In such a furnace two charges may be worked off in twenty-four hours. During the operation the small adapters, n, n, are withdrawn once in two hours, and the liquid zinc which has condensed in the receivers is raked out into a large ladle and cast into ingots. When the distillation is complete, the residues in the retorts still retain nearly 25 per cent. of zinc, which is chiefly in the form of silicate of the oxide; this portion is entirely wasted. (Piot and Muraille, *Ann. des Mines*, IV. v., 165.)

The retorts in the upper part of such a furnace necessarily receive less heat than those in the lower part, and hence this process is particularly well adapted to the Belgian ores, because the poorer ones, which require less heat, can be employed in charging the upper retorts.

(589) Commercial zinc contains a small quantity of lead, iron, and of a peculiar carbonaceous matter. The best method of obtaining the metal in a state of purity consists in transmitting sulphuretted hydrogen through a slightly acidulated solution of sulphate of zinc, filtering from any precipitate which may be formed; and after boiling the solution in order to expel the sulphuretted hydrogen, precipitating the zinc in the form of carbonate by the addition of carbonate of soda. The carbonate, when ignited, is converted into oxide of zinc, which must be distilled in a porcelain retort with charcoal prepared from loaf sugar.

(590) *Properties.*—Zinc is a hard, bluish-white metal, which when a mass of it is broken across exhibits a beautiful crystalline fracture. It is brittle at ordinary temperatures, but between  $200^{\circ}$  and  $300^{\circ}$ , it is possessed of considerable ductility and malleability, and may be laminated and wrought with ease: at a temperature a little higher than this it again becomes so brittle that it may be pulverized in a mortar. It fuses at  $773^{\circ}$ , and at a bright red heat it may be volatilized: if its vapour be exposed to the air, it burns with great splendour and is converted into oxide, which is deposited in copious white flocculi. It soon tarnishes when exposed to a moist atmosphere, and becomes covered with a thin, closely-adhering film of oxide, by which the metal beneath is protected from further change. This property renders zinc valuable for a variety of economical and domestic purposes. It is, however, readily attacked by all the mineral acids, and is employed to

decompose dilute sulphuric acid when hydrogen is required. Boiling solutions of potash also act upon zinc, hydrogen is liberated, whilst oxide of zinc is formed and dissolved in the alkaline solution;  $\text{Zn} + \text{H}_2\text{O}, \text{KO} = \text{H} + \text{ZnO}, \text{KO}$ .

(591) The uses of zinc are daily extending. From its durability, cheapness, and lightness, it is frequently employed as a substitute for lead in roofing. Sheet-iron coated with zinc, or *galvanized* iron as it is often called, is also used for the same purposes; the iron gives strength, whilst the zinc protects it from oxidation, and it is not combustible like zinc alone.

Galvanized iron is prepared by cleaning sheet-iron thoroughly as in making tin plate (675), and plunging the metal into a bath of molten zinc, covered with sal ammoniac; the surface of the zinc is by this means kept free from oxide, which is dissolved by the sal ammoniac, and the two metals readily unite. A tougher and superior article is obtained by first coating the iron plate with a very thin film of tin by a voltaic action, and then immersing the metal into the melted zinc.

Zinc has a considerable power of dissolving iron, in consequence of which it corrodes the iron pots in which it is melted: an alloy of zinc with a small proportion of iron is formed, which is less fusible than zinc, and crystallizes in large plates on cooling.

Zinc forms several valuable alloys. Of these brass is the most important: it consists of about 2 parts of copper to 1 of zinc. German silver is brass containing a portion of nickel, to which its white colour is due. Of late years zinc in powder has been employed as the basis of a pigment well adapted to resist the action of the weather. The oxide of zinc, under the name of *zinc white*, has also been employed as a substitute for white lead, to form the basis of a white paint; but it wants the opacity and dead whiteness for which the carbonate of lead is so much valued. Oxide of zinc has likewise been substituted for red lead with great advantage in the preparation of glass for optical purposes (499).

(592) *Oxide of Zinc* ( $\text{ZnO}$ ): *Eg.* 405.—Zinc forms only one compound with oxygen, which is regarded as a protoxide. This oxide is occasionally deposited in furnace flues in yellowish, six-sided prisms; but it is generally obtained in the form of a white flocculent powder. If zinc be thrown in small quantities at a time into a capacious clay crucible previously heated to whiteness, it burns with a brilliant flame and deposits large white flakes of the oxide; but when thus prepared, it is mechanically mixed with particles of the metal, from which it may be separated by levigation with water; the heavier metallic portions quickly subside and leave the oxide

in suspension. The process of manufacturing this oxide when it is required as a pigment, consists in distilling zinc from clay retorts into chambers through which a current of air is maintained. The volatilized metal burns at the high temperature to which it is exposed under these circumstances, and the oxide is deposited in a series of condensing chambers. An impure oxide, sold under the name of *tutty*, is obtained from the flues of furnaces in which brass is melted.

Oxide of zinc becomes yellow when heated, but recovers its whiteness as the temperature falls. The hydrated oxide is precipitated from the solutions of the salts of zinc by the addition of potash or soda; it is redissolved by an excess of the alkaline liquid.

(593) *Sulphide of Zinc; Blende* ( $\text{ZnS}$ ); *Eq.* 48.5; *Sp. Gr.* 4.1. —This compound is one of the most abundant minerals of zinc: when pure it is of a pale brown colour, but generally it is nearly black from admixture with sulphide of iron. It usually crystallizes in rhombic dodecahedra, but it occurs in other forms of the regular system. Metallic zinc does not readily unite with sulphur: but if rapidly heated in mixture with cinnabar, (or sulphide of mercury,) the mercury is volatilized and sulphide of zinc is formed with almost explosive violence. Sulphide of zinc does not fuse when heated: when roasted in the air it absorbs oxygen; at a low temperature a large portion of it is converted into sulphate of zinc, but at a higher temperature sulphurous acid is formed, and oxide of zinc is left. Nitric acid and aqua regia dissolve it readily. When the salts of zinc are mixed with hydrosulphate of ammonia, a white, gelatinous, hydrated sulphide of zinc is precipitated, which absorbs oxygen quickly from air, and is readily dissolved by acids.

(594) *Chloride of Zinc* ( $\text{ZnCl}$ ); *Eq.* 68. —This salt is obtained by dissolving the metal in hydrochloric acid; the acid is decomposed, its chlorine unites with the zinc, whilst its hydrogen escapes in the gaseous form: the chloride of zinc dissolves. When this solution is heated it loses water till the temperature rises to  $480^{\circ}$ ; it then becomes anhydrous, but remains fluid, and may be heated above  $700^{\circ}$  F. without emitting an inconvenient amount of fumes; hence it is frequently employed as a hot-bath for maintaining objects at a high but measurable and regulated temperature. At a red heat it distils. Pure chloride of zinc is a white, very deliquescent substance, fusible at about  $212^{\circ}$ ; it is powerfully corrosive when applied to the skin. It is soluble in alcohol.

Chloride of zinc absorbs ammoniacal gas freely. Several oxychlorides of zinc may be formed. Chloride of zinc forms double

salts with the chlorides of the alkaline metals; a concentrated solution of the double chloride of zinc and ammonium ( $\text{H}_4\text{NCl} + \text{ZnCl}$ ) is used for the purpose of removing the film of oxide from the surface of metals, such as zinc, iron, or copper, which are to be united by the operation of soldering.

(595) *Sulphate of Zinc* ( $\text{ZnO}$ ,  $\text{SO}_3$ , 7 aq, Eq.  $80.5 + 63$ , Sp. Gr., anhydrous, 3.681, crystallized, 1.931), is obtained in large quantities as a residue in the ordinary process of procuring hydrogen by the action of dilute sulphuric acid. It may also be prepared by roasting sulphide of zinc at a low temperature, lixiviating the mass and crystallizing. It crystallizes in colourless, four-sided prisms, which constitute the white vitriol of commerce. In a dry air it is efflorescent; it dissolves in two parts and a half of water at  $60^\circ$ , and melts in its own water of crystallization when heated. Sulphate of zinc is used medicinally in small doses; it is also prepared largely for the calico printer.

(596) *Carbonate of Zinc* ( $\text{ZnO}$ ,  $\text{CO}_2$ , Eq.  $62.5$ , Sp. Gr.  $4.4$ ), is found native in various forms, usually of a greyish or yellowish colour, forming one variety of *calamine*, which is so named from its property of adhering, after fusion, in the form of reeds, to the base of the furnace. No neutral carbonate of zinc can be obtained from its salts by double decomposition. When a hot solution of a salt of zinc is precipitated by a boiling solution of an alkaline carbonate, a hydrated oxycarbonate is formed, consisting of ( $8 \text{ ZnO}$ ,  $3 \text{ CO}_2 + 6 \text{ aq}$  Schindler). Several other basic carbonates of zinc may be formed.

The other variety of calamine becomes electric by heat; it is a hydrated subsilicate; ( $2 \text{ ZnO}$ ,  $\text{SiO}_2 + \text{aq}$ ).

(597) **CHARACTERISTICS OF THE SALTS OF ZINC.**—The salts of zinc are colourless; their solutions have a styptic, metallic taste, and act rapidly and powerfully as emetics.

They are distinguished by giving no precipitate in acid solutions with *sulphuretted hydrogen*; a white sulphide of zinc with *hydrosulphate of ammonia*; a white hydrated oxide with *potash*, *soda*, or *ammonia*, soluble in excess of the alkali; a white, basic carbonate of zinc with the *alkaline carbonates*; and a white precipitate with *ferrocyanide of potassium*.

*Before the blowpipe*, in the reducing flame on charcoal, the metal is reduced and volatilized, burning into white fumes of oxide of zinc. If placed on charcoal and moistened with solution of nitrate of cobalt the compounds of zinc when heated leave a green, unfused residue.

(598) *Estimation of Zinc in analysis.*—Zinc is best precipitated for analysis by carbonate of potash, the whole solution being evaporated down to dryness; the residue, which contains the carbonate of zinc, is washed with boiling water, dried, and converted by ignition into oxide of zinc, which is weighed. The oxide contains, in 100 parts, 80.26 of zinc and 19.74 of oxygen. If ammoniacal salts be present, a sufficient excess of the carbonate of potash should be used completely to decompose the salts of ammonia, the ammonia being wholly expelled as carbonate of ammonia during the process of evaporation. The foregoing process is not applicable to the separation of zinc from any but the alkaline bases.

(599) *Separation of Zinc from the Alkalies and Alkaline Earths.*—This may be effected by the addition of hydrosulphate of ammonia to the solution after it has been neutralized by ammonia; the zinc is thus precipitated as sulphide; it must be washed with a solution of sulphuretted hydrogen to prevent its oxidation, then redissolved in hydrochloric acid and evaporated to dryness with excess of carbonate of soda: the soluble salts must be washed from the carbonate of zinc, which is to be converted into oxide by ignition, and then weighed.

*The separation of Zinc from Alumina and Glucina* may be effected by dissolving all the bases by means of an excess of caustic potash, and adding hydrosulphate of ammonia; in this case sulphide of zinc is alone precipitated; it may be collected and its amount determined in the manner just described.

## § II. CADMIUM.

*Symbol, Cd; Equivalent, 56.74; Specific Gravity, 8.6.*

(600) CADMIUM is occasionally found as sulphide of cadmium, accompanying zinc in its ores, and is obtained as an accidental product during the extraction of the latter metal. Being more volatile than zinc, the greater part of the cadmium sublimes among the first portions of the distilled metal, from which it may be extracted by dissolving them in sulphuric acid, and precipitating the cadmium as sulphide by means of sulphuretted hydrogen; the sulphide may be dissolved in strong hydrochloric acid, precipitated by carbonate of ammonia, and reduced in an earthen retort by ignition with charcoal; the metal distils over at a heat below redness.

Cadmium is of a white colour, resembling tin, and like it creaks when a rod of it is bent; it is so soft that it leaves its traces upon paper, and possesses considerable malleability and ductility.



Cadmium fuses at  $442^{\circ}\text{F.}$ , and may be obtained in octohedral crystals as it cools. In the atmosphere it undergoes little change, but when thrown into a red-hot crucible it takes fire, depositing brownish yellow fumes of oxide. It is dissolved with evolution of hydrogen when heated in sulphuric or hydrochloric acid slightly diluted; nitric acid, also, dissolves it freely.

(601) The *oxide* ( $\text{CdO}$ ; *Eg.* 677, *Sp. Gr.* 6.93) is obtained as a brown anhydrous powder, by burning the metal; it is not fusible or volatile in the furnace. A white hydrated oxide of cadmium may be obtained by decomposing its salts by a fixed alkali; ammonia in excess redissolves it, but potash and soda have no such effect: even the anhydrous oxide is soluble in ammonia. Carbonate of ammonia does not dissolve oxide of cadmium either in the anhydrous or hydrated form.

The *Sulphide* ( $\text{CdS}$ , *Eg.* 767), may be formed by transmitting a current of sulphuretted hydrogen through a solution of a salt of cadmium; it greatly resembles orpiment in appearance, but is distinguished from it by its want of volatility when heated, and by its insolubility in ammonia and in the alkaline sulphides.

(602) CHARACTERS OF THE SALTS OF CADMIUM.—The salts of cadmium are colourless, and resemble those of zinc: the chloride crystallizes easily. They may be readily distinguished by the yellow precipitate of sulphide of cadmium which they yield with *sulphuretted hydrogen* in acid solutions; this precipitate is insoluble either in ammonia or in the alkaline sulphides. *Potash and soda* give a precipitate of white hydrated oxide, insoluble in excess; *ammonia*, a similar precipitate, very soluble in excess; *carbonates of potash, soda, and ammonia*, a white carbonate, insoluble in excess; *oxalic acid*, a white precipitate, soluble in ammonia; *ferrocyanide of potassium*, a yellowish-white precipitate, soluble in hydrochloric acid. *Before the blowpipe* they are decomposed, and a ring of brown oxide of cadmium is deposited on the cool part of the charcoal, due to the reduction and subsequent combustion of the metal.

*Estimation of Cadmium.*—Cadmium is readily separated from all the foregoing metals by the action of sulphuretted hydrogen, which causes a precipitate of the yellow sulphide of cadmium from an acidulated solution of its salts. This precipitate is redissolved in nitric acid, decomposed by an excess of carbonate of soda, evaporated to dryness, washed from the soluble salts, and the resulting carbonate of cadmium is heated to redness, and converted into oxide and weighed; 100 grains of oxide of cadmium contain 87.45 of the metal.

## § III. COBALT.

*Symbol, Co ; Equivalent, 29.49 ; Specific Gravity, 8.95.*

(603) COBALT generally occurs, in combination with arsenic, as speiss cobalt or tin white cobalt ( $\text{CoAs}$ ), but occasionally it is found as *cobalt glance*, which is a compound of the arsenide and the sulphide of the metal ( $\text{CoS}_2, \text{CoAs}$ ). Cobalt is never met with in the native state, except as an ingredient in meteoric iron in small proportion. The black oxide has been found to some extent in the Western States of America, mixed with the sulphide of cobalt and with variable proportions of the oxides of nickel, manganese, iron, and copper. The ores of this metal occur chiefly in the primitive rocks, and are usually very complicated; containing nickel, iron, and often bismuth and copper, mineralized either by sulphur or by arsenic, or by both together.

Cobalt is not used in the metallic state in the arts. Many of the compounds of cobalt are remarkable for the beauty and brilliancy of their colour.

It is not easy to obtain the metal in a state of purity. On a small scale the ore may be treated as follows:—It is first roasted at a low but gradually rising temperature, in order to expel the greater portion of the arsenic; after which it is dissolved in aqua regia, and evaporated to dryness to expel the excess of acid; it is then redissolved in water, and a current of sulphuretted hydrogen is transmitted through the solution. Bismuth, copper, and the remainder of the arsenic are thus precipitated as sulphides. The filtered liquid is boiled to expel the excess of the gas, and a slight excess of nitric acid is added to the boiling liquid, to peroxidize the iron; when cold, it is diluted and supersaturated with ammonia; the peroxide of iron is precipitated, carrying with it a little cobalt, but the bulk of the cobalt remains dissolved with any nickel which the ore may have contained.

The exact separation of cobalt from nickel is tedious. Two methods have been proposed, one by Rose, the other by Liebig (617). Rose's method is the following:—The two metals are thrown down from the ammoniacal liquid as sulphides, by the addition of hydrosulphate of ammonia. The sulphides are redissolved in nitric acid, the solution is then largely diluted, and acted upon by a current of chlorine; after this it is digested in a closed vessel for 12 hours upon powdered carbonate of baryta. The chlorine converts the cobalt into sesquioxide, which is gradually precipitated by the baryta, and remains mixed with the excess of car-

bonate of baryta employed. This precipitate is again dissolved in nitric acid; the baryta removed by adding sulphate of soda, and the oxide of cobalt precipitated by caustic soda: the precipitate is well washed with boiling water, and reduced in a current of hydrogen gas, which leaves the metal in the form of a black, highly magnetic powder. When nickel is to be separated from cobalt for the purposes of analysis, Mr. Henry recommends the substitution of a solution of bromine for chlorine gas in the foregoing process. Bromine may be used instead of chlorine in many analogous cases with great convenience.

If oxide of cobalt be reduced in a crucible lined with charcoal, a carbide of cobalt is formed, which may be obtained in a well fused button. The crucible may be lined with charcoal for this purpose by dipping it into water, and filling it completely with charcoal finely powdered, and sufficiently moistened to render it coherent when firmly beaten into the crucible; a cylindrical cavity is then scooped out of the middle of the mass, and its interior is carefully smoothed with a glass rod, after which the crucible is allowed to dry slowly. Pure cobalt may also be procured by heating the oxalate in a covered porcelain crucible, enclosed in a second earthen one, with the cover luted down; the crucibles are then exposed for an hour to the most intense heat of a forge: a well fused button of cobalt may generally be obtained in this manner.

Metallic cobalt is nearly as infusible as iron. It is of a reddish grey colour; is hard, brittle, and strongly magnetic. It dissolves slowly, with evolution of hydrogen, in hydrochloric and dilute sulphuric acids, and it is freely oxidized by nitric acid; when exposed to the atmosphere it becomes slowly converted into oxide.

The alloys of cobalt are unimportant. Its compounds with arsenic are interesting, as they supply the greater part of the cobalt employed in the arts. *Tin white cobalt*, when pure, contains an equivalent of each of the two metals ( $\text{Co As}$ ), but portions of the cobalt are frequently displaced by nickel and iron. The purest specimens of this mineral are obtained from Tunaberg; the ore from this locality is the best material to employ in preparing the compounds of cobalt. Arsenide of cobalt melts at a moderate red heat. *Bright white cobalt*, or *cobalt glance* ( $\text{CoS}_2 + \text{CoAs}$ ), corresponds in composition to mispickel: it crystallizes in cubes, octohedra, or dodecahedra.

(604) *Oxides of Cobalt*.—There are two well marked oxides of cobalt, the protoxide  $\text{CoO}$ , which is the only salifiable base of the metal, and the sesquioxide ( $\text{Co}_2\text{O}_3$ ); these two oxides are capable of uniting with each other in different proportions.

*Protoxide* ( $\text{CoO}$ ), *Eq.* 37.5.—This oxide is of an ash grey colour; when heated in the air it absorbs oxygen, and becomes black. It is soluble in acids, and forms solutions which, when concentrated, are of a beautiful blue colour, but they become pink on dilution. The oxide forms an important article of commerce, from its employment for the production of a blue colour in painting on porcelain. When describing the preparation of nickel, a process will be detailed which furnishes the oxide of cobalt fit for this purpose.

The *zaffre* of commerce is a very impure oxide of cobalt, procured by imperfectly roasting cobalt ore, mingled with 2 or 3 parts of siliceous sand.\*

*Smalt* is a beautiful blue glass coloured by oxide of cobalt; it is chiefly manufactured in Saxony. In preparing smalt, the cobalt ore is first roasted; but the roasting is arrested at a particular stage, the object being to oxidize the cobalt, whilst the nickel, copper, and iron remain in combination with arsenic and sulphur; it is necessary to leave a sufficient amount of arsenic in the mass, to retain these metals, as the admixture of a very small quantity of the oxides either of iron, nickel, or copper with the glass seriously injures the purity of its colour. From 4 to 5 parts of the roasted ore in powder are next mingled with 10 parts of ground calcined quartz, and 4 parts of carbonate of potash, and the mixture is slowly melted in pots arranged in a furnace resembling that used in making ordinary glass. The oxide of cobalt combines with the fused silicate of potash; a deep blue glass is thus formed, whilst the mixed arsenides and sulphides of nickel, copper, and iron fuse and collect at the bottom of the pot, in the form of a brittle mass, of metallic appearance, commonly known as *speiss*. The pot is then skimmed, and the glass is ladled out, and poured into cold water, by which means it is split into innumerable fragments: the *speiss* is cast into ingots and used in the manufacture of nickel. The broken glass is stamped to powder, and subsequently ground between granite stones, which are caused to revolve under water in a vessel, through which a gentle stream of water is continually flowing. The water as it flows off carries with it the powdered smalt in suspension: it is made to pass through a number of depositing vessels, so arranged that the overflow from the first shall pass into the second, that from the second into the third, and so on: each of these vessels is successively larger than the one which precedes it, so that the period for which the washings are retained in each goes on progressively increasing, and the particles deposited progressively increase in the minuteness of their subdivision; the colour becoming less intense, the greater the degree of subdivision of its particles.

Smalt is used largely by paper-stainers, to produce a blue colour, and it is employed to some extent by laundresses, for correcting the yellow tinge in linen.

Another valuable pigment into the composition of which cobalt enters is of a pale blue colour, and is known as *Thénard's blue*. The most approved method of preparing it, consists in precipitating nitrate of cobalt by means of phosphate of potash, and mixing the precipitate whilst still moist with four or five times its bulk of the gelatinous mass obtained by adding carbonate of soda to a dilute solution of alum perfectly free from iron. The mixture is dried and then exposed to a dull red heat in a covered crucible. The brilliancy of the colour is much impaired by the reducing action of the combustible gases of the fuel. The best preventive of this effect is found to consist in placing a little red oxide of mercury at the bottom of each crucible; by the decomposition of this oxide an atmosphere of oxygen is obtained, and the metallic mercury is dissipated in vapour (Regnault, *Traité*, vol. iii. p. 150).

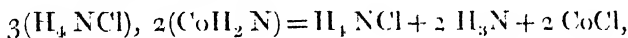
*Rinman's green* is a pigment of analogous composition, containing oxide of cobalt combined with oxide of zinc.

Hydrated oxide of cobalt ( $\text{HO}$ ,  $\text{CoO}$ ), is precipitated by the addition of potash or soda to solutions of any of its salts. The pale blue precipitate which is first formed is a subsalt of cobalt, but if an excess of alkali be used, it quickly becomes violet, and finally rose-coloured, which is the true colour of the hydrated oxide: these changes occur most rapidly if the liquid be warmed. This hydrated oxide is readily dissolved by solution of carbonate of ammonia, and also by excess of ammonia, especially in the presence of a neutral ammoniacal salt.

*Sesquioxide of Cobalt* ( $\text{Co}_2\text{O}_3$ , *Eq.* 83), may be prepared by suspending the hydrated protoxide of the metal in water, and transmitting a current of chlorine through the liquid; chloride of cobalt is formed and dissolved, whilst a black hydrated sesquioxide of cobalt is precipitated,  $\text{Co}_2\text{O}_3$ , 3  $\text{HO}$ . The reaction may be thus expressed:  $3 \text{CoO} + \text{Cl} = \text{Co}_2\text{O}_3 + \text{CoCl}$ . If the oxide of cobalt be suspended in a solution of potash instead of in pure water, the whole of the cobalt is precipitated as sesquioxide. Sesquioxide of cobalt does not combine with acids: it may be rendered anhydrous by a careful application of heat, but if strongly heated it becomes converted into a black oxide ( $\text{CoO}$ ,  $\text{Co}_2\text{O}_3$ ), corresponding with the magnetic oxide of iron. It is, however, difficult to obtain this oxide of a fixed composition, as by a strong heat the sesquioxide which it contains is liable to partial decomposition,

and the compound is thereby contaminated with a variable quantity of the protoxide of cobalt.

(605) *Ammoniacal Compounds of Cobalt*.—When a solution of a salt of cobalt in ammonia is exposed to the air, it absorbs oxygen rapidly, although the hydrated protoxide of cobalt alone exhibits no such tendency. If the hydrated oxide be dissolved in an ammoniacal solution of chloride of ammonium, the absorption of oxygen proceeds quickly, and a remarkable violet-red colour gradually develops itself in the liquid. If at this stage the liquid be supersaturated with hydrochloric acid and boiled, a heavy crimson powder precipitates, leaving the solution colourless; this precipitate may be dissolved in water slightly acidulated with hydrochloric acid, and as the liquid cools, beautiful rusty-red octohedral crystals are formed. According to F. Claudet (*Quart. Jour. Chem. Soc.* iv. 357), they contain the elements of  $3 \text{H}_4 \text{NCl}$ ,  $2 \text{CoH}_2 \text{N}$ . This remarkable compound is quite insoluble in boiling hydrochloric acid, and may be employed as a means of obtaining chemically pure cobalt: at a red heat it loses ammonia and hydrochlorate of ammonia, leaving chloride of cobalt;—



and the chloride of cobalt may be reduced to the metallic state by passing a current of hydrogen gas over it in a tube heated to redness. When digested with water upon oxide of silver, the chlorine is withdrawn from the new compound, whilst the oxygen of the oxide takes its place;\*

$3(\text{H}_4 \text{NCl}), 2(\text{CoH}_2 \text{N}) + 3 \text{AgO} = 3(\text{H}_4 \text{NO}), 2(\text{CoH}_2 \text{N}) + 3 \text{AgCl}$ ; a red strongly alkaline liquid is thus produced, which unites with acids, and forms a peculiar class of salts: this alkaline solution emits no smell of ammonia.

Freymy, in an elaborate series of researches on the ammoniacal compounds of cobalt, has shown (*Ann. de Chimie*, III. xxxv. 257) that, independent of the ammoniacal compounds obtained with the ordinary salts of the metal, and of the compounds described by Claudet, three other sets of salts may be procured, which he regards as compounds of different oxides of cobalt with various proportions of ammonia: the first of these bases he names *oxyco-baltia*. Its salts crystallize readily, and dissolve in solution of

\* Both Freymy and Rogojski (*Ann. der Chemie*, III. <sup>XLV</sup> 456), who have recently examined this compound, have given reasons for supposing that it contains 1 equivalent less of hydrogen than has been assigned to it by Claudet.

ammonia without change, but when placed in cold water they are decomposed with evolution of oxygen and deposition of a green subsalt: the salts of this base appear to contain a binoxide of cobalt, which, however, cannot be isolated. The second base, from the yellow colour of its salts, he terms *luteocobaltia*; this base has been isolated; it has a strong alkalinic reaction, and its salts crystallize easily. The third base is termed *fuscobaltia*; it forms brown uncrystallizable salts. The base of Claudet's salts Fremy terms, from the red colour of its compounds, *rosecobaltia*. For details regarding the preparation of these different compounds, the reader is referred to the memoir already quoted.

All the compounds of each of these four bases, when boiled with solutions of caustic potash or of soda, are decomposed, and hydrated sesquioxide of cobalt ( $\text{Co}_2\text{O}_3, \text{H}_2\text{O}$ ), is precipitated, whilst ammonia is expelled.

The following table will afford a general comparative view of these different classes of salts, including the double salts which ammonia forms with the protoxide of the metal:—

1. *Double Salts of Ammonia and Protoxide of Cobalt.*

Nitrate . .  $\text{CoO}, \text{NO}_5, 3 \text{H}_3\text{N}, 2 \text{HO}$

Chloride . .  $\text{CoCl}, 3 \text{H}_3\text{N}, 3 \text{HO}$

2. *Salts of Oxykobaltia.*

Nitrate . .  $2(\text{CoO}_2, \text{NO}_5), 5 \text{H}_3\text{N}, 2 \text{HO}$

Sulphate . .  $2(\text{CoO}_2, \text{SO}_3), 5 \text{H}_3\text{N}, 3 \text{HO}$

3. *Salts of Luteocobaltia.*

Nitrate . .  $\text{Co}_2\text{O}_3, 3 \text{NO}_5, 6 \text{H}_3\text{N}$

Chloride . .  $\text{Co}_2\text{Cl}_3, 6 \text{H}_3\text{N}$

4. *Salts of Fuscobaltia.*

Nitrate . .  $\text{Co}_2\text{O}_3, 2 \text{NO}_5, 4 \text{H}_3\text{N}, 3 \text{HO}$

Chloride . .  $\text{Co}_2\text{Cl}_2\text{O}, 4 \text{H}_3\text{N}, 3 \text{HO}$

5. *Salts of Rosecobaltia (Claudet's Salts).*

Nitrate . .  $\text{Co}_2\text{O}_3, 3 \text{NO}_5, 5 \text{H}_3\text{N}$

Chloride . .  $\text{Co}_2\text{Cl}_3, 5 \text{H}_3\text{N}, \text{HO}$

(606) *Compounds of Cobalt with Sulphur.*—Three sulphides of this metal may be obtained,—a protosulphide,  $\text{CoS}$ , a sesquisulphide,  $\text{Co}_2\text{S}_3$ , and a bisulphide,  $\text{CoS}_2$ . The most important of these is the *protosulphide*, which may be procured by precipitating

a solution of acetate of cobalt by sulphuretted hydrogen, or by mixing any neutral solution of a salt of cobalt with hydrosulphate of ammonia. In this form it speedily absorbs oxygen from the air, and becomes converted into sulphate of cobalt. If a mixture of oxide of cobalt be fused with persulphide of potassium (the liver of sulphur) in a covered crucible, a fused sulphide of cobalt is obtained at the bottom of the crucible.

(607) *Chloride of Cobalt*, ( $\text{CoCl}$ , *Eq.* 65, *Sp. Gr.* 2.937), is obtained as a lilac-coloured anhydrous mass by passing chlorine over metallic cobalt; it is volatile at a high temperature. By dissolving the oxide of cobalt in hydrochloric acid, the hydrated chloride may be obtained in ruby-red octohedral crystals, which are readily soluble in water and alcohol; its aqueous solution when concentrated is of a deep blue colour, but on dilution it becomes pink. This dilute solution may be used as a sympathetic ink; characters traced with it on paper, though invisible when cold, become blue by heat, and again fade as the hygroscopic moisture of the paper is restored from the air: the colours of this ink may be varied at pleasure; the addition of a small proportion of a salt of peroxide of iron renders it green; zinc produces a red, and copper a yellow tint.

The *Sulphate of Cobalt* ( $\text{CoO}$ ,  $\text{SO}_3 + 7 \text{ aq}$ , *Eq.* 77.5 + 63, *Sp. Gr. anhydrous* 3.531), is isomorphous with sulphate of magnesia.

*Nitrate of Cobalt* ( $\text{CoO}$ ,  $\text{NO}_5 + 6 \text{ aq}$ , *Eq.* 91.5 + 154), is prepared by dissolving the oxide in nitric acid. It is a deliquescent salt which is sometimes employed as a reagent for the blowpipe; a fragment of the compound under examination is supported either upon charcoal, or upon a bent platinum wire, and moistened with a minute quantity of a strong solution of the nitrate of cobalt. When treated in this way, many of the compounds of magnesia yield a pale pink-coloured mass after ignition; those of oxide of zinc give a green residuc, and those of alumina a blue.

If a concentrated solution of nitrite of potash be gradually added to a solution of nitrate of cobalt acidulated with nitric acid, a beautiful orange yellow compound is precipitated: it is sparingly soluble, and, according to St. Evre, by whom it was discovered, consists of  $2(\text{KO}, \text{NO}_3 + \text{CoO NO}_5) + \text{aq}$ .

A hydrated *arseniate* of cobalt,  $(3 \text{ CoO}, \text{As}_2\text{O}_5 + 8 \text{ aq})$  is found native, and is known as *cobalt bloom*.

(608) *Carbonates of Cobalt*.—Cobalt resembles magnesia, zinc, and nickel, in the circumstance that when solutions of its neutral salts are mixed with a solution of carbonate of soda or potash, the precipitate which falls is not a neutral carbonate, but a mixture of



neutral carbonate with hydrated oxide of cobalt. If the two solutions be mixed when hot, the red precipitate is said to have the formula  $(5 \text{ CoO}, 2 \text{ CO}_2, 4 \text{ aq})$ . If the salts be mixed at the ordinary temperature, the precipitate is of a brighter red, and has a composition  $(4 \text{ CoO}, 2 \text{ CO}_2 + 7 \text{ aq})$ . If either of these precipitates be boiled with an excess of carbonate of soda, it assumes an indigo blue colour, and is converted into the compound  $4 \text{ CoO}, \text{ CO}_2, 4 \text{ aq}$ , which absorbs oxygen, and becomes green during washing.

A true neutral carbonate,  $3(\text{CoO}, \text{CO}_2) 2 \text{ aq}$ , is formed by digesting either of the basic carbonates of cobalt with bicarbonate of soda or ammonia.

(609) **CHARACTERS OF THE SALTS OF COBALT.**—The crystallized salts of cobalt are red; when anhydrous they are usually lilac. Their solutions when in a very concentrated form are blue; at a particular stage of dilution they are red when cold, but become blue on heating them, the red colour returning as the liquid cools: when mixed with a larger proportion of water they exhibit a delicate rose colour, and this tint is perceptible even when the solution is very much diluted. They have an astringent metallic taste.

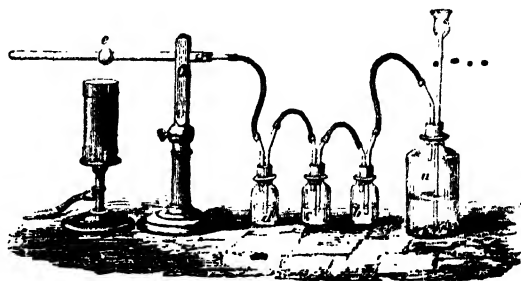
*Before the blowpipe* the compounds of cobalt are recognised by the intense blue colour which they communicate to a bead of borax in the oxidating flame.

In solution the salts of this metal give no precipitate with *sulphuretted hydrogen*, if the liquid be slightly acidulated with sulphuric or hydrochloric acid. With *hydrosulphate of ammonia* they yield a black sulphide. *Carbonate of potash* gives a rose-coloured basic carbonate, which is soluble in carbonate of ammonia. *Potash* gives a blue subsalt, which by excess of the alkali becomes rose-coloured. *Ammonia* produces a similar effect, but readily dissolves the precipitate, forming a reddish solution which rapidly absorbs oxygen from the air, and becomes green. The soluble *oxalates* give a sparingly soluble pink oxalate of cobalt, which is soluble in nitric acid and in ammonia. *Ferrocyanide of potassium* gives a dirty green, and *ferridcyanide of potassium* a bulky reddish brown precipitate.

(610) **Estimation of Cobalt.**—Cobalt can only be estimated with accuracy in the metallic form. Supposing that no compound of any other metal susceptible of precipitation by hydrosulphate of ammonia be present, except cobalt, the solution is to be neutralized and then mixed with hydrosulphate of ammonia, taking care to add as small an excess of the hydrosulphate as possible; the liquid is

next to be warmed, the precipitate allowed to settle in a beaker closed by a glass plate, then collected on a filter, and washed with water containing a little sulphuretted hydrogen. The alkalis are prevented from effecting the complete precipitation of cobalt, as well as of iron, of nickel, of copper, and of many other metals, by the presence of certain kinds of organic matter, such as that derived from the paper of the filter; special precautions are therefore required to avoid this accident. For this purpose the neck of the funnel with the filter and its contents is introduced into a small flask, a hole is made with a glass rod in the bottom of the filter, and the precipitate is washed into the flask; the filter after being moistened with concentrated nitric acid, is again washed; it is then dried, burnt, and the ash added to the contents of the flask, which are now boiled with nitric acid until the sulphide of cobalt is dissolved. The liquid thus obtained is diluted and poured off from any particles of undissolved sulphur. The cobalt thus brought into solution by the nitric acid is precipitated in the form of hydrated oxide by an excess of potash; the oxide is thoroughly washed with boiling water, dried, ignited, and weighed. The amount of cobalt cannot be safely inferred from the weight of this oxide, as it consists of a mixture of protoxide and sesquioxide of cobalt in variable proportions. The oxide is therefore reduced in a current of dry and pure hydrogen in the manner shown in fig. 304. The tube, *e*, is weighed when

FIG. 304.



empty; then a certain proportion of the oxide of cobalt is introduced in the bulb, and the tube is again weighed; hydrogen is generated in the bottle, *a*, and allowed to traverse the apparatus; *b* contains a solution of potash, and *c* one of nitrate of silver, which are designed to arrest any traces of arseniuretted hydrogen; oil of vitriol is placed in *d* for the purpose of drying the gas: a dull red heat is next applied to the bulb, *e*, and as soon as water ceases to form, the reduction is complete: the lamp is then removed from the bulb, but the current of hydrogen is maintained till the tube is quite cold. The tube and its contents are then weighed a third

time, and the proportion of metallic cobalt which a given weight of the oxide under trial contained, is thus ascertained.

(611) *Separation of Cobalt from the Alkalies and Alkaline Earths, and from Alumina.*—This is readily effected by the addition of hydrosulphate of ammonia to the solution previously neutralized by ammonia. If alumina be present, it will accompany the cobalt, but if this precipitate be redissolved in acid, and again thrown down by means of caustic potash in excess, the alumina will be retained; the oxide of cobalt is, however, apt to carry down traces of alumina; these may be removed by treating the precipitated oxide by means of a mixture of ammonia and chloride of ammonium, which dissolves the cobalt, but leaves any traces of alumina which may have accompanied it. The cobalt is again precipitated by hydrosulphate of ammonia.

*The separation of Cobalt from Zinc* is not easy. One of the best methods consists in precipitating the metals together in the form of sulphides, dissolving this precipitate in nitric acid, and then adding an excess of carbonate of potash, and evaporating to dryness. After the mixed carbonates of zinc and cobalt have been well washed, they are heated in a bulb tube in a current of dried hydrochloric acid. The open end of the tube is in this case bent downwards at a right angle, and the aperture is made to dip into a small quantity of water contained in a flask; the chloride of zinc, which is volatile, is carried forward in the current of gas, a portion of it is condensed in the bend of the tube, and the remainder is dissolved in the water placed for its reception. Chloride of cobalt alone remains in the bulb. The portion of the tube in which the chloride of zinc has been condensed is cut off when the operation is complete, and is allowed to fall into the flask. The zinc and the cobalt are then easily determined separately by the usual methods.

#### § IV.—NICKEL.

*Symbol, Ni; Equivalent, 29.54; Specific Gravity, 8.82.*

(612) NICKEL is a metal, the peculiar characters of which were first recognised in 1751, by Cronstedt; it has a remarkable analogy to cobalt, and always occurs associated with it in nature, both as a constituent of meteoric iron, and in its ores, which present a composition analogous to those of cobalt. It is most abundant in the form of kupfernickel, which is a diarsenide of nickel, and is

extracted either from this ore or from speiss, which is an impure arseniosulphide of nickel, formed during the manufacture of smalt.

As the metal itself is now extensively used in alloys, of which German silver is one of the most important, great pains have been taken to procure it in a state of comparative purity, and several processes have been proposed. According to Lonyet, the process by which nickel is extracted from speiss at Birmingham on the large scale is as follows:—The speiss is first fused with chalk and fluorspar, the metallic mass obtained is reduced to powder, and roasted for twelve hours to expel the arsenic; the residue is then dissolved in hydrochloric acid; the solution is diluted, and the iron peroxidized by the cautious addition of bleaching powder. Milk of lime is then carefully added so long as peroxide of iron falls, which carries down with it the last portions of arsenic: this precipitate is well washed, and the liquid which contains all the cobalt and nickel is treated with a current of sulphuretted hydrogen; the sulphides of copper, bismuth, and lead, are thus precipitated, and are thoroughly washed. All the nickel and cobalt still remain in the liquid; this liquid is again treated with chloride of lime: the whole of the cobalt is thus thrown down as peroxide; after which the whole of the nickel is separated from the solution in the form of hydrated oxide by adding milk of lime as long as any precipitate is produced.

Nickel may be obtained pure upon a small scale, by dissolving the roasted ore in aqua regia, evaporating to expel the excess of acid, redissolving in water, and transmitting a current of sulphuretted hydrogen. The filtered liquid is boiled with nitric acid, to peroxidize the iron; the solution is precipitated by an excess of caustic ammonia, filtered from the oxide of iron, and to the blue liquid caustic potash is added until the blue tint nearly disappears; a pale green precipitate, consisting of hydrated oxide of nickel and potash is thus obtained, which must be well washed with hot water to remove the potash, and then reduced by ignition in a current of hydrogen gas. If heated for an hour by means of a blacksmith's forge, in a crucible lined with charcoal, a well-fused button of carbide of nickel is produced. A button of the pure metal may however be procured by heating the oxalate of nickel intensely in a crucible with a luted cover, without any other reducing agent than the carbonic oxide furnished by its own decomposition.

Pure nickel is a brilliant, silver white, ductile metal, little more fusible than iron. At ordinary temperatures it is susceptible of magnetism, but it loses this property almost entirely if heated to a

point exceeding  $630^{\circ}$  F., though it recovers its magnetic power on cooling. Nickel becomes oxidized by exposure to a current of air at a high temperature. The metal is easily attacked by nitric acid and aqua regia, and is dissolved slowly with evolution of hydrogen in sulphuric or in hydrochloric acid. Owing to the remarkable whitening power which nickel exerts on brass, it is now much used in the manufacture of *packfong*, or German silver, a compound of zinc, nickel, and copper, in which the proportions of the metals may vary considerably. A good alloy consists of 5 equivalents of copper, 3 of zinc, and 2 of nickel, or in 100 parts, of 51 of copper, 30.6 of zinc, and 18.4 of nickel. Packfong is of a yellowish white colour, and when freshly polished closely resembles silver in appearance.

The native arsenides of nickel are important, as they form the principal ores of the metal. *Kupfernickel* ( $\text{Ni}_2\text{As}$ ) is a combination containing 44 parts of nickel to 56 of arsenic; part of the arsenic is sometimes displaced by an equivalent amount of antimony. *Arsenical nickel* is a combination of an equivalent of each metal ( $\text{NiAs}$ ): by ignition in close vessels it loses half its arsenic, and becomes converted into kupfernickel. A compound of nickel with arsenic and sulphur, corresponding to mispickel, and known as *nickel glance* ( $\text{NiS}_2 + \text{NiAs}$ ), is also found native.

(613) *Compounds of Nickel with Oxygen*.—Nickel forms two oxides: a protoxide,  $\text{NiO}$ , and a sesquioxide,  $\text{Ni}_2\text{O}_3$ .

*The Protoxide* ( $\text{NiO}$ , *Eq.* 37.5), may be obtained in the anhydrous form by igniting the carbonate of the metal in a covered crucible, when it is left of an olive green colour. It may be precipitated from its salts by potash, as a bulky light green hydrate, ( $\text{NiO}, \text{HO}$ ), and may be obtained crystallized by boiling carbonate of nickel in solution of ammonia. Oxide of nickel forms insoluble compounds with potash or soda, which, however, may be decomposed by frequent washings with boiling water. Baryta, strontia, and several other bases, also form with it insoluble compounds; ammonia dissolves it, forming a deep blue solution; when fused with borax, the oxide colours the glass of a hyacinth yellow, which becomes less intense as it cools.

*The Sesquioxide* ( $\text{Ni}_2\text{O}_3$ , *Eq.* 83), is a black powder which may be procured by treating the hydrated protoxide with solution of chloride of soda. It does not combine with acids, and gives off a portion of its oxygen by ignition, or by heating with nitric or sulphuric acids, which form with it salts of the protoxide.

(614) *Sulphide of Nickel* ( $\text{NiS}$ , *Eq.* 45.5), occurs native in greyish or yellowish capillary crystals: it may be formed artificially

by fusion, and can be obtained as a black hydrate when a salt of nickel is precipitated by sulphide of ammonium. It may also be procured by fusing an alkaline persulphide with arsenide of nickel, and is left in yellow crystalline scales. A *disulphide* ( $\text{Ni}_2\text{S}$ ) has been formed by reduction of the sulphate of nickel by means either of charcoal or of hydrogen gas.

*Chloride of Nickel* ( $\text{NiCl}$ , *Eq.* 65), is formed by dissolving the oxide in hydrochloric acid. Its solution, on evaporation, yields green hydrated crystals; by heat it may be obtained as a yellowish brown anhydrous mass, which at a high temperature is volatile, and condenses in yellow crystalline scales, which dissolve slowly in water.

*Sulphate of Nickel* ( $\text{NiO}$ ,  $\text{SO}_3$  7 aq), *Eq.* 77·5 + 63, *Sp. Gr. cryst.* 2·037.—This salt crystallizes in green rhombic prisms, which, when exposed to light, are converted without loss of water into small regular octohedra, aggregated together in the form of the original crystal, which becomes opaque. It may be obtained in octohedra at once by crystallizing at a temperature between  $60^\circ$  and  $80^\circ$  F. A *double sulphate of potash and nickel* ( $\text{NiO}$ ,  $\text{SO}_3$  +  $\text{KO}$ ,  $\text{SO}_3$  + 6 aq, *Sp. Gr. cryst.* 2·190, *dry* 2·897), may be formed by adding potash to the impure solution of speiss, and by repeated crystallizations may be freed from all impurities except traces of iron and cobalt: it was at one time used as a means of purifying nickel for commercial purposes. Other double sulphates of nickel may be formed.

*Carbonates of Nickel.*—There are several basic carbonates of nickel, of a green colour. The neutral carbonate precipitates as a crystalline powder, when a solution of nitrate of nickel is poured into a large excess of bicarbonate of soda.

(615) CHARACTERS OF THE SALTS OF NICKEL.—The salts of this metal are of a delicate green colour, both when in the solid state and when in solution. They have a sweetish astringent metallic taste, and when taken internally excite vomiting.

*Before the blowpipe* salts of nickel give in the oxidating flame with borax, a reddish yellow glass, which becomes much paler as it cools. In the reducing flame greyish particles of reduced nickel are disseminated through the bead.

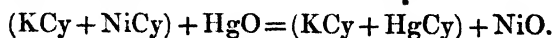
In solution *sulphuretted hydrogen* gives no precipitate if the liquid be acidulated with sulphuric acid. *Hydrosulphate of Ammonia* gives a black sulphide. *Ammonia* gives a pale green precipitate, soluble in excess of ammonia, forming a bright blue solution. *Potash and Soda* throw down a pale green bulky

hydrated oxide of nickel. The *carbonates of the alkalis* give a pale apple green precipitate of basic carbonate of nickel, which is readily soluble in carbonate of ammonia. *Ferrocyanide of potassium* gives a greenish white, and *ferridcyanide of potassium* a yellowish green, precipitate.

(616) *Estimation of Nickel*.—Nickel is best estimated in the form of protoxide, which, when precipitated by means of potash, requires patient washing with hot water to remove the adhering alkali: 100 parts of protoxide of nickel contain 78.69 of the metal.

*Separation of Nickel from the Alkalies and Earths, and from Zinc*.—For this purpose the same processes as those adopted for the separation of cobalt (611) may be employed.

(617) *Separation from Cobalt*.—The method advised by Liebig for this purpose is the best. The cobalt and nickel having been freed from all other substances except salts of potash or soda, are precipitated in the form of hydrated oxides, which after partial washing from the adhering alkaline salts, are mixed with caustic potash and a decided excess of hydrocyanic acid; the mixture is then boiled for ten minutes in order to expel the greater part of the excess of hydrocyanic acid, and to convert the oxides into double cyanides of cobalt and nickel. A cobalticyanide of potassium,  $(K_3Co_2Cy_6)$ , is formed, attended with escape of hydrogen; a double cyanide of nickel and potassium,  $(KCy + NiCy)$  is produced at the same time. The formation of the cobalticyanide may be traced as follows: cyanide of cobalt is first formed,  $HCy + CoO = CoCy + HO$ , and this cyanide of cobalt, by boiling with an excess of cyanide of potassium and hydrocyanic acid, yields cobalticyanide of potassium and free hydrogen,  $2 CoCy + 3 KCy + HCy = (K_3Co_2Cy_6) + H$ . The double cyanide of nickel and potassium is very simply formed, as with nickel no compound corresponding to the cobalticyanide is obtained;  $2 KCy + NiO = (KCy + NiCy) + HO$ . If the solution be now boiled with very finely levigated oxide of mercury, the nickel salt is decomposed, hydrated oxide of nickel is precipitated, and cyanide of mercury is produced:—



The cobalticyanide of potassium is not decomposed by the oxide of mercury, but remains in solution, and may be filtered from the oxide of nickel, which requires to be carefully ignited in a platinum crucible till it ceases to lose weight. The cobalt may then be precipitated from the filtrate as a white subcobalticyanide of mercury by the addition of solution of subnitrate of mercury; the precipitate is collected, dried, and ignited, when pure oxide

of cobalt is left, which may be reduced to the metallic state in a current of hydrogen.

### § V. URANIUM.

*Symbol*, U ; *Equivalent*, 60.

(618) URANIUM is a metal the compounds of which are but sparingly distributed over the surface of the earth. It was originally discovered by Klaproth, in pitchblende, which contains nearly 80 per cent. of the black oxide of uranium ( $2\text{UO}$ ,  $\text{U}_2\text{O}_3$ ); the remainder of the mass consists of variable quantities of copper, lead, iron, arsenic, and frequently of cobalt and nickel. *Uranite*, which is a mineral of micaceous structure, of rarer occurrence, consists of a hydrated double phosphate of lime and uranium : ( $\text{CaO}$ ,  $2\text{U}_2\text{O}_3$ ,  $\text{PO}_5$ , 8 aq). *Chalcolite* is a similar mineral, in which oxide of copper takes the place of lime.

In order to extract uranium from pitchblende, the mineral is heated to redness and thrown whilst red-hot into water, after which it admits of being readily pulverized : Ebelmen advises that the ore should then be treated in the following manner :—The fine powder is to be washed with dilute hydrochloric acid, heated with charcoal, and digested in strong hydrochloric acid, by which the earthy matters and most of the iron, arsenic, and sulphur are removed ; the washed residue is to be roasted and then treated with nitric acid ; the solution is evaporated nearly to dryness and diluted : arseniate of iron is thus precipitated. Sulphuretted hydrogen is then to be transmitted through the filtered solution ; the liquid is next to be filtered from the sulphides of copper, lead, and arsenic thus formed ; it is again evaporated, until crystals of permuriate of uranium begin to form. This salt is to be decomposed by heating it to redness, and the oxide of uranium which is left is to be mingled with charcoal and heated in a glass tube through which a current of dry chlorine is passing ; carbonic acid and carbonic oxide are formed, and a volatile green protochloride of uranium sublimes. This chloride when heated with potassium in a platinum crucible yields chloride of potassium and metallic uranium : intense heat is evolved during the reaction of the potassium on the chloride of uranium, and the resulting metal is partially fused. The isolation of metallic uranium is due to M. Peligot (*Ann. de Chimie*, III. v., 5), the substance originally supposed to be the metal having been proved by him to be its protoxide.

Uranium as thus obtained is of white colour : it appears to be slightly malleable : it is not oxidized by exposure to air or to



water at ordinary temperatures; but if heated in the air it burns brilliantly: sulphuric and hydrochloric acids dissolve it with extrication of hydrogen gas. In its chemical relations it is closely analogous to iron and manganese.

(619) *Compounds of Uranium with Oxygen.* — Uranium forms two principal oxides, a *protoxide*,  $\text{UO}$ , and a *sesquioxide*,  $\text{U}_2\text{O}_3$ : two intermediate oxides may also be obtained, the *black oxide*,  $2 \text{UO} + \text{U}_2\text{O}_3$ , and the *green oxide*,  $\text{UO} + \text{U}_2\text{O}_3$ .

The *Protoxide* ( $\text{UO}$ , *Eq.* 68) may be obtained in several ways, one of the easiest consists in igniting the ~~per~~<sup>sesqui</sup>oxalate in close vessels. In its anhydrous state the dilute acids are without action upon it, but its hydrate dissolves readily, forming green crystallizable salts.

The *Black Oxide* ( $2 \text{UO} + \text{U}_2\text{O}_3$ ) may be procured by heating the protoxide to bright redness, and suddenly cooling, or by igniting the pernitrate of uranium. It furnishes a pure and intense black, highly prized for colouring porcelain.

The *Green Oxide* ( $\text{UO} + \text{U}_2\text{O}_3$ ) is procured by heating the black oxide moderately in a current of oxygen or in the open air; by more intense ignition it becomes re-converted into the black oxide, and again is partially re-oxidized as it cools. It is soluble in hot concentrated sulphuric acid, but does not form distinct salts.

The *Sesquioxide* ( $\text{U}_2\text{O}_3$ ) performs the part both of an acid and of a base. It is with difficulty obtained in a pure state. By exposing the peroxalate of uranium to the sun's rays a brownish-violet powder, a hydrate of the green oxide, is deposited, while carbonic acid makes its escape; this precipitate absorbs oxygen on exposure to the air, and becomes converted into a greenish-yellow mass, which according to Ebelmen is a hydrate of the sesquioxide ( $\text{U}_2\text{O}_3, 2 \text{aq}$ ). The sesquioxide may be obtained in the anhydrous state as a brick-red powder by heating this hydrate to a temperature not exceeding  $572^\circ \text{F}$ . Peroxide of uranium combines readily with acids, and forms salts of a bright yellow colour. If an attempt be made to procure the peroxide by decomposing the solutions of these salts by the addition of an alkali, an insoluble yellow precipitate, a uranate of the base falls, which cannot be decomposed even by boiling water: the commercial oxide is a hydrated uranate of ammonia, from which heat expels the water and ammonia, and also converts the peroxide into the black or the green oxide. Its compounds with the earths, however, stand a strong heat without decomposition, and are employed to communicate a beautiful and peculiar yellow to glass.

(620) *Protochloride of Uranium* ( $\text{UCl}$ ) is a green, volatile deliquescent compound, which is decomposed by water; the method of preparing it has already been described (618). If dry hydrogen gas

be transmitted over the protochloride of uranium while it is being heated to redness in a glass tube, a *subchloride* ( $U_4Cl_3$ ) is produced, which crystallizes in slender dark-brown needles, which are but slightly volatile; they are very soluble in water, and form a deep purple solution. Ammonia throws down a brown suboxide, which rapidly absorbs oxygen from the air. An *oxychloride* ( $U_2ClO_2$ ), or ( $2 U_2O_3 + U_2Cl_3$ ), is formed by passing chlorine over the protoxide of the metal; it is deliquescent, and forms a yellow solution with water; with the alkali chlorides it forms remarkable double salts; the double salt with chloride of potassium consists of ( $KCl, U_2ClO_2 + 2 aq$ ) and crystallizes in rhombic tables of a greenish-yellow colour.

(621) CHARACTERS OF THE COMPOUNDS OF URANIUM.—1. The salts of the protoxide of uranium have a green colour, and have a strong tendency to form double salts with salts of the alkaline metals which contain the same acid as themselves. *Ammonia* and the *alkalies* give a gelatinous, blackish-brown precipitate of hydrated oxide, which absorbs oxygen and becomes yellow from the formation of sesquioxide of uranium, which unites with the excess of alkali. *Sulphuretted hydrogen* produces no precipitate; but *hydrosulphate of ammonia* occasions a black deposit of sulphide of uranium. *Oxalate of ammonia* gives a greenish-white precipitate of oxalate of uranium. Solutions of the green salts of uranium rapidly absorb oxygen, and are converted by nitric acid into persalts, even without the aid of heat.

2. The salts of the peroxide are yellow, and all of them contain, even when crystallized from strongly acid solutions, 1 equivalent only of sesquioxide to 1 equivalent of the acid. The pernitrate, for instance, which crystallizes in long striated prisms, consists of ( $U_2O_3, NO_5, 6 aq$ ). Numerous double salts of this oxide have also been formed: the persulphate of uranium and potash consists of ( $KO, SO_3 + U_2O_3, SO_3 + 2 aq$ ). The persalts of uranium give with *ammonia* a yellow precipitate, consisting of uranate of ammonia; with *ferrocyanide of potassium* they yield a hair-brown precipitate. By the action of ammonia they are distinguished at once from the compounds of copper, which give a blue solution on the addition of an excess of ammonia, though they yield a precipitate with the ferrocyanide similar in colour to that furnished by the salts of uranium. *Sulphuretted hydrogen* produces no precipitate, but *hydrosulphate of ammonia* gives a yellowish-brown sulphide. *Carbonates of the alkalies* give a yellow, granular precipitate, soluble in excess of the precipitant; these precipitates are double carbonates of uranium and of the alkali employed. With *infusion of nut galls* a dark-brown precipitate is produced.

(622) *Estimation of Uranium.*—Uranium is usually estimated in the form of protoxide, to which it is reduced by heating the sesquioxide to redness in a glass tube in a current of hydrogen; the tube must be sealed up whilst full of hydrogen, and weighed in this condition, to prevent the oxide from reabsorbing oxygen from the air.

Uranium is separated from the alkalis by converting it into a persalt by nitric acid, if not already in that condition, and then precipitating it in the form of yellow uranate of ammonia. If baryta, strontia, lime, or magnesia be present, the addition of sulphuric acid separates the first two bases in the form of sulphates; if lime or magnesia be present, the solution is filtered from the precipitate, the filtrate evaporated to dryness, and then heated with alcohol of specific gravity 0.900; the sulphate of lime and magnesia remain unacted upon, whilst the persulphate of uranium is dissolved.

Alumina, glucina, zinc, cobalt, and nickel, may be separated from uranium by adding bicarbonate of potash to the acidulated solution: a double carbonate of potash and uranium remains in the liquid, whilst the earths, and other metallic oxides, are precipitated. For the success of this experiment it is necessary, if the salts of ammonia be present, that they should be expelled, by evaporating the solution to dryness and igniting the residue before effecting the precipitation of the various bases with bicarbonate of potash.

## § VI. IRON.

*Symbol, Fe; Equivalent, 28; Specific Gravity, 7.844.*

(623) *Condition of Iron in Nature.*—IRON is more extensively diffused than any other metal: not only is it abundant in the inorganic creation, but it is an essential constituent in the blood of the vertebrate animals.

Iron has been occasionally found in the native form accompanying the ores of platinum; but when it occurs in the metallic state it is generally met with in meteoric masses associated with nickel, cobalt, and small quantities of other metals, among which are copper, manganese, and chromium. Some of these masses which have fallen in an ignited state from the atmosphere are of very considerable size. One discovered in Siberia, by Pallas, weighed 1600 lb., and a block found in the district of Chaco-Gualamba, in South America, is estimated at between thirteen and fourteen tons weight. These extraordinary bodies are unimportant as sources of iron.

The ores of iron are numerous. The most valuable are the following:—

1. *Magnetic Iron Ore* ( $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ), *Sp. Gr.* 5.09, or loadstone;

this is found in enormous masses, or even mountains, amongst the primary formations. Much of the best Swedish iron is obtained from this material, which is also abundant in North America. Occasionally it is found in detached octohedral crystals.

2. *Specular Iron Ore, or Fer Oligiste, Sp. Gr. 5.2.*—This is an anhydrous sesquioxide of iron ( $\text{Fe}_2\text{O}_3$ ): it occurs in the primary rocks. The principal part of the celebrated Elba iron, and also a large quantity of Russian and of Swedish iron, are obtained from this source.

3. *Red Hematite* ( $\text{Fe}_2\text{O}_3$ , *Sp. Gr.* about 5.0), is another form of the anhydrous peroxide: it is sometimes found massive, but more generally in fibrous crystalline nodules. This ore is largely raised in Lancashire and in some parts of Cornwall.

4. *Brown Hematite* ( $2 \text{Fe}_2\text{O}_3, 3 \text{H}_2\text{O}$ ), *Sp. Gr.* about 3.9.—This is a hydrated peroxide of iron, which generally occurs massive. It is, however, also met with in the oolitic strata in some parts of France, in the form of rounded masses termed *pea iron ore*, mixed with a small proportion of clay. Much of the French iron is obtained from this source. Brown hematite is readily soluble in hydrochloric acid; it is less refractory in the furnace than the preceding variety, which is seldom worked alone, but generally in mixture with other ores. The brown hematite, when roasted becomes porous from the loss of its water, and is thus rendered more manageable. Mixed with variable proportions of earth or clay this oxide of iron forms the varieties of unker and ochres. It occurs principally in the secondary and tertiary deposits.

5. *Spathic Iron, or Carbonate of Iron* ( $\text{FeCO}_3$ ), *Sp. Gr.* 3.8.—This is found in crystalline masses often combined with carbonate of magnesia and with a considerable proportion of manganese, as in the Saxony ores. Much of this so-called *natural steel* is made from this ore.

6. *Clay Ironstone* is the chief source of the enormous quantity of iron manufactured in Great Britain. It is an impure carbonate of iron, containing generally from 30 to 33 per cent. of metallic iron, mingled with varying proportions of clay, oxide of manganese, lime, and magnesia. This argillaceous ironstone occurs in bands broken up into nodules, or in continuous seams, from two to fourteen inches thick, alternating with beds of coal, clay, shale, or limestone, in the coal measures diffused over large areas in South Staffordshire, South Wales, and some other parts of Great Britain. It is also found in the United States, and in Bohemia and other countries of central Europe. It has a specific gravity ranging between 2.7 and 3.4.

7. *The Black Band* of the Scotch coal fields is also a carbonate of iron, but the principal foreign matter in this mineral is of a bituminous or combustibile nature.

8. A siliceous ironstone, occurring in the oolite in the neighbourhood of Northampton, has been found to a large extent, and is now beginning to be worked.

9. Another, but comparatively an unimportant ore, of a brown colour, known as *bog-iron ore*, is a mixture of hydrated peroxide and of phosphate of iron in variable proportions. It occurs in marshy, alluvial districts, near the surface.

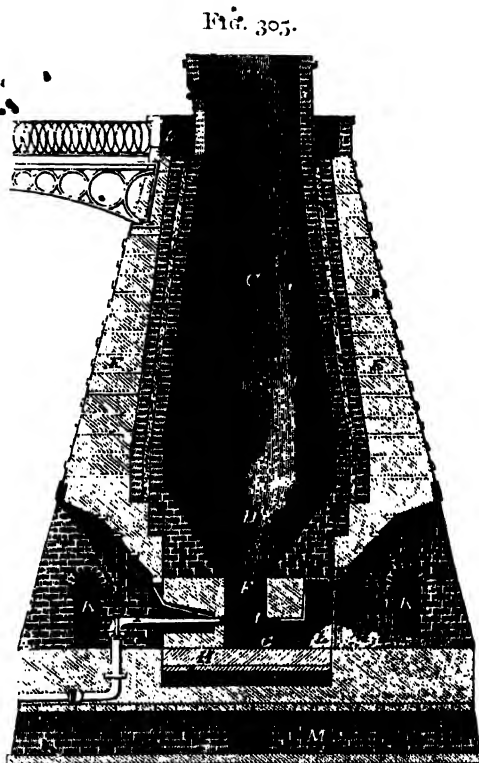
Iron pyrites ( $\text{FeS}_2$ ), though a very abundant mineral, is wrought only for the sake of its sulphur, as the iron which it furnishes is not pure enough for use.

#### SMELTING OF CLAY IRONSTONE.

(624) After the ore has been broken up into masses about the size of two fists, it is roasted, in order to expel water and carbonic acid; the mass is thus left in a porous state, highly favourable to its subsequent reduction in the furnace. The roasting is sometimes performed in kilns, but usually in heaps in the open air. If this operation is to be effected in the open heap, a plat of ground is levelled and covered with a layer of coal in lumps to the depth of ten or twelve inches; this is succeeded by alternate layers of the mineral and of small coal. The quantity of coal required in the case of the black band is often very small, as the ore itself frequently contains sufficient inflammable matter to continue burning when once well lighted. The heap, when finished, is fourteen or fifteen feet wide, eight or ten high, and of great length. The fire is kindled at the windward extremity, and allowed to spread gradually through the mass. This preliminary operation occupies some months for its completion. The roasted ore is then ready for the smelting. The *blast furnace* employed for this purpose is represented in section in fig. 305. The internal cavity in shape resembles a long narrow funnel inverted upon the mouth of another shorter funnel. These furnaces are usually about 50 feet high, and from 14 to 17 feet in diameter in the widest part of the cavity. The lowest portion, or neck of the funnel, is termed the *crucible*, and is made of very refractory gritstone. In the front, eight or ten inches from the floor or *hearth*, H, is a longitudinal aperture above the *tymp-stone*, L, for the overflow of the slag, and on the sides are the opening for the *tuyères*, I I, or blast-pipes, which are connected with powerful blowing machines for supplying air under a pressure of from two to three pounds upon the inch.

A steady and most intense heat is thus uniformly maintained. At the lowest point of the furnace is the *tap-hole*, for drawing off the melted metal at suitable intervals, and which, except at such times, is closed with sand and clay: *κ κ*, are galleries, which allow the workmen free access to the tuyères and lower portion of the furnace, the base of which is kept dry and well drained by the arched channels, *μ*. Above the

crucible the furnace suddenly widens, forming the *boshes*, *ν*; the lining, *ς*, is formed of fire-bricks, which are continued up to the throat, *α*, of the furnace: the whole is cased in solid masonry, *ε ε*, and supported by iron bands. When working regularly, such a furnace is charged through the opening, *β*, near the top, at intervals, first with coal, and then with a suitable mixture of roasted ore and of a limestone flux broken into small fragments. As the fuel burns away, and the materials gradually sink down, fresh layers of fuel, and of ore, are added; so that the furnace becomes filled with alternate layers of fuel and of ore.



The principal substances which are acted upon in such a furnace are the following:—

1st, The oxygen contained in the air of the blast; 2nd, the roasted ore,—consisting of oxide of iron, silica in the shape of sand or quartz, clay or silicate of alumina, and a little magnesia and oxide of manganese; 3rd, coal or coke,—composed chiefly of carbon, with a small proportion of hydrogen; and 4th, carbonate of lime, which in the heat of the furnace soon becomes quick lime.

(625) The chemical changes may be traced as follows, beginning at the bottom of the furnace:—The oxygen contained in the air of the blast, as soon as it comes into contact with the fuel in the

crucible, combines with the carbon and forms carbonic acid, attended with a combustion of intense activity. The blast is thus soon deprived of all its free oxygen; nearly the whole of the nitrogen escapes unchanged, but the carbonic acid, in its passage over the ignited fuel, is decomposed; it combines with an additional equivalent of carbon, and becomes converted into carbonic oxide; for each volume of carbonic acid 2 volumes of carbonic oxide are produced. This formation of carbonic oxide is attended with a large absorption of heat, so that the temperature of the furnace, above the crucible, becomes rapidly reduced, and a quantity of highly combustible gas is thus formed.\* This carbonic

Bunsen and Playfair, in their examination of the gases produced in a hot blast furnace at Alfreton, found that a considerable amount of cyanide of potassium was formed in the hotter portions of the furnace (*British Association Reports*, 1845, p. 182); part of the nitrogen, derived probably both from the blast and from the coal, had therefore entered into combination with carbon, and had united with the potassium contained in small quantities in the ore and in the ashes of the coal.

The furnace in which these experiments were made was 40 feet deep from the top of the charge to the hearthstone, and was charged every twenty minutes with 420lb of ironstone, 390lb of coal, and 170lb of limestone: each charge yielded 140lb of pig iron. The blast was under a pressure of 6·75 inches of mercury.

These chemists state that at a depth of two feet and three-quarters from the tuyère, or 34 feet from the top of the furnace, the gases which they collected contained 1·34 per cent. of cyanogen. The following table furnishes a summary of the results which they obtained:—

*Analysis of Gases from a Hot-blast Furnace.*

Depth from the top Height from tuyère .	5 feet. 32	8 29	14 23	17 20	20 17	24 13	34 2½
Nitrogen . . . . .	55·35	54·77	50·95	55·49	60·46	56·75	58·05
Carbonic acid . . . .	—7·77	9·42	9·10	12·43	10·83	10·08	0·00
Carbonic oxide . . . .	25·97	20·24	19·32	18·77	19·48	25·19	37·43
Light Carb. Hyd. . . .	3·75	8·23	6·64	4·31	4·40	2·33	0·00
Hydrogen . . . . .	6·73	6·49	12·42	7·62	4·83	5·65	3·18
Elefant gas . . . . .	0·43	0·85	1·57	1·38	0·00	0·00	0·00
Cyanogen . . . . .	0·00	0·00	0·00	0·00	0·00	trace	1·34
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

The process of coking, which takes place in the upper part of the furnace, did not appear to be complete until the charge had reached a depth of 24 feet, but was most active at a depth of 14 feet; the principal reduction of the ore seemed to occur just below the point at which the coking was completed; the maximum heat of this furnace occurring between about 3 and 4 feet above the tuyère, or 32 feet from the top.

In a furnace fed with charcoal, Bunsen found the reduction of the ore to commence nearer the throat of the furnace; as in this case no absorption of heat occurred similar to that occasioned by the process of coking the coal, which takes place in the upper part of the hot-blast furnace. The body of a charcoal furnace consequently does not require to be so high as that of a furnace in which coal is used. Similar experiments by Ebelmen lead to conclusions substantially the same.

oxide becomes mingled with carburetted hydrogen and free hydrogen, which are derived from the fuel contained in the upper part of the charge, as it gradually descends towards the focus of intense heat below. A proportion of the gases which escape from the opening at the top of the furnace, varying from 35 to 40 per cent., is combustible; the remainder consists principally of nitrogen, with a small amount of carbonic acid. The ore having been rendered porous by the previous roasting, is easily penetrated by these ascending gases, by contact with which the iron becomes reduced in the upper part of the boshes, where the heat is comparatively moderate. By degrees the reduced metal, mixed with the earthy matter of the ore, sinks down to the hotter region. Here the earthy matters melt and become vitrified; whilst the iron, in a minutely divided state, being brought into contact with the carbon of the fuel, combines with it and forms the fusible compound well known as cast-iron. This carbide of iron melts, sinks down below the tuyères through the lighter vitrified slags, and is protected by them from the further action of oxygen. The bulk of the slag is five or six times as great as that of the iron produced: it floats above the melted metal, and is allowed to flow over continually at the opening left for the purpose; whilst the iron is run off at intervals of 12 or 24 hours, by withdrawing the stopping of clay or sand from the tap-hole at the bottom.

The furnace slags constitute an imperfect species of glass, consisting principally of silicates of lime, magnesia, and alumina, with generally a small proportion of silicate of manganese. In the formation of these slags the siliceous matters of the ore act like a true acid, as they combine with the earthy bases, lime, magnesia, and alumina, and really neutralize them.

The general composition of these slags may be seen from the subjoined analysis, by Berthier, of a slag from Merthyr Tydvil:—

Silica	. . . . .	40·4
Lime	. . . . .	38·4
Magnesia	. . . . .	5·2
Alumina	. . . . .	11·2
Oxide of Iron	. . . . .	3·8
Sulphur	. . . . .	traces
		<hr/>
		99·0

The composition of this slag may therefore be represented by the formula,  $5 [3(\text{CaMgFe})\text{O}, 2 \text{SiO}_2] + 2(\text{Al}_2\text{O}_3, \text{SiO}_2)$ .

The iron as it runs from the furnace, however, is not a pure



carbide or carburet, for in the intense heat, not only is the iron reduced, but portions also of silicon, aluminum, and calcium, and occasionally other bodies, derived from the flux and from the fuel. These bodies enter in minute quantity into combination with the iron, the properties of which they materially modify. Manganese generally accompanies the ores of iron in greater or less quantity, and frequently combines with the reduced metal.

There are several points which require nice adjustment in this process of reduction. The slag must not be of too fusible a description, otherwise the iron falls to the bottom before it has thoroughly combined with the carbon, and is not completely melted; a sufficiency of lime should always be present to neutralize the whole of the silica, for unless this be attended to a silicate of iron is formed, and runs off in waste. Indeed, a small excess of lime is advantageous, as it removes sulphur, if present, in the shape of sulphide of calcium. At the same time the calcareous matter must not be too abundant, otherwise the working of the furnace is obstructed; the slags which are formed being of a less fusible character are but imperfectly melted, the iron is entangled within them, it is again partially oxidated by the blast, and the product of the furnace is greatly diminished. Experience has shown that the slags are most fusible when the oxygen of the silica amounts to double that in the bases with which it is combined; and slags containing several bases are more fusible than when one or two only are present, the different silicates aiding the fusibility of each other.

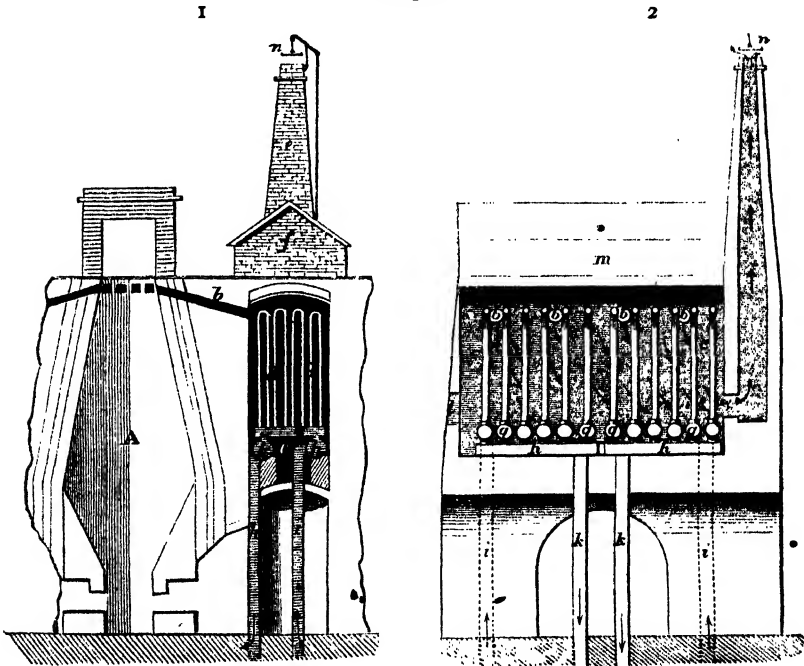
It is also necessary to proportion the supply of air rightly; if too much be thrown in, the furnace becomes unduly cooled; if too little, the supply of oxygen is insufficient for the maintenance of a proper temperature by a due amount of combustion. These, however, are points, the successful regulation of which can only be acquired by experience.

The stream of air for the blast is not supplied in intermitting gusts, but is equalized as much as possible: where the cold blast is used this object is attained by employing an air chamber or reservoir; and where the hot blast is employed, the long pipes required for heating the air answer the same purpose.

(626) *The Hot Blast*.—The mass of air which passes through one of these furnaces is enormous, being not less than 6 tons weight per hour. It is evident, therefore, that this immense volume of air must exercise an extraordinary cooling effect upon the contents of the furnace. This evil has been much reduced of

late years by the introduction of air which has been previously heated. In this contrivance, which is known as the *hot blast*, the air, before it reaches the furnace, is made to pass through a series of pipes which are maintained at a high temperature, either by means of a separate furnace, or by a portion of the waste heat of the blast furnace itself: in the latter case the hot gases are conveyed through flues which pass from the upper part of the furnace into the chamber which contains the pipes; the necessary draught being maintained by a chimney furnished with a damper. Fig. 306 shows the plan adopted by Mr. Budd of the Ystalyfera Works,

FIG. 306.



South Wales, for applying the waste gases of the furnace to the heating of the blast. In No. 1, *A* represents a section of the blast furnace, *b* one of the tubes which carries off the heated gases into a brickwork chamber *m*, *f*, shown in cross section in No. 1, and in longitudinal section in No. 2; *d d* are pipes through which the blast is forced, in order that it may be heated; it enters the heating apparatus through *i i*, passes through the pipes *g* and *h* into *d d*, and makes its escape in a heated condition through the pipes *k k* to the tuyères 1, 1, fig. 305. The gases from the furnace take the

course indicated by the arrows, through the chamber, and escape by the chimney *e*, which is surmounted by a damper, *n*; *l* is a man-hole, which is opened only when it is necessary to enter the chamber for the performance of repairs. A jet of the escaping blast should have a temperature sufficiently high to melt a strip of lead when held in it. The temperature of such a jet, as it issues from the tuyère, is somewhat higher than 600° F. The saving of fuel effected by the employment of the hot blast is immense, and is much greater than was at first anticipated: 2½ tons of coal are now amply sufficient for the production of a ton of iron, from ore which would have required 8 tons when the cold blast was used. This saving is effected owing to the operation of several causes, one of which is, that raw coal may now be used in the furnace instead of coke: moreover, as a smaller quantity of fuel is required in the furnace to raise the injected air to the necessary temperature, so also a smaller quantity of air is needed to maintain the combustion: the maximum heat of the furnace is obtained lower down in the "crucible," so that the upper portions of the furnace do not become so intensely heated: the reduction of the ore consequently takes place nearer to the bottom, and the heat is thus concentrated and economized. In the year 1845, the hot blast was used in every furnace in Scotland, with the exception of one at the Carron Works, and it was computed that the change from the cold to the hot blast had effected a saving of coal in that country alone amounting to 2,000,000 tons annually. (*North Brit. Review*, No. vii., p. 128.) Even in a hot blast furnace, however, the quantity of fuel which is wasted is enormous. MM. Bunsen and Playfair, from their elaborate experiments at Alfreton, make the almost incredible estimate that somewhat more than ¼ths of the total quantity of heat producible from the fuel consumed is lost, owing to the escape of unburned combustible matter in the form of gases, such as carbonic oxide, carburetted hydrogen, and hydrogen, which are still fit for use. Since the publication of these researches, Mr. Budd and other iron-masters have economized a portion of the heat contained in the escaping gases, in heating the blast, and in generating steam.

The iron obtained by the use of the hot blast is inferior in tenacity to cold blast iron; a circumstance which is easily accounted for by the fact, that in the employment of the hot blast uncoked coal is used, a fuel which contains more sulphur, and probably also more phosphorus than coke, which is required in working with the cold blast. Mr. Crace Calvert, of Manchester, has recently introduced a method of purifying the fuel, which

promises considerably to ameliorate the quality of pig-iron, by diminishing the quantity of sulphur which it is liable to retain. It enables him also to employ coal which, on account of the large proportion of pyrites which it contains, could not formerly be used for iron smelting. His process consists in mixing from 1 to  $2\frac{1}{2}$  per cent. of chloride of sodium with the coal previous to coking, the proportion of the salt being varied according to the quantity of pyrites present in the coal. He has also found, that if the same proportion of chloride of sodium be added to the raw coal, and the mixture be charged at once into the blast furnace, results are obtained almost equally satisfactory. The sulphur appears to be expelled in the form of chloride of sulphur.

A furnace in full work requires an hourly supply of rather more than  $1\frac{1}{2}$  tons of solid material, consisting on an average of 5 parts of coal, 5 of roasted ore, and 2 of limestone. The roasted clay iron ore yields on an average 40 per cent. of iron, and each furnace when in full activity furnishes from 8 to 10 tons of metal in the 24 hours. Every morning and evening it requires to be tapped: on these occasions the iron is run into shallow grooves in the sand, and forms the cast-iron, or pig-iron of commerce. A good furnace if well managed may be made thus to work uninterruptedly without repair for many years.\*

(627) *Composition and Properties of Cast-Iron.* — Cast-iron differs greatly in quality; the differences observed in it depend in part upon differences in the proportion of carbon and silicon which it contains. The composition of these carbides differs greatly within certain limits; but it does not appear that iron is capable of combining with more than about 5 per cent. of carbon. A compound of carbon having the composition of  $\text{Fe}_3\text{C}$  would consist of 94.92 of iron, and 5.08 of carbon; and this is very nearly the composition of the hardest kind of white cast-iron, which from the circumstance of its crystallizing in flat, brilliant tables, is termed by the Germans *spiegeleisen* (or mirror iron). Faraday and Stodart found the most highly carburetted iron which they could produce, to consist of—iron, 94.36; carbon, 5.64. In many varieties of cast-iron the carbon exists in two distinct forms,—one portion, being chemically combined with the metal, the other being me-

\* The production of iron in Great Britain in 1851, amounted to about 2,500,000 tons. It was stated in 1845 (*North British Review*, Nov., 1845, p. 134), on the authority of Mr. Goldenberg, of Berlin, that the production of iron in different countries in Europe was then as follows. England 1,500,000 tons, France 350,000, Russia 320,000, Germany 150,000, Austria 100,000, Belgium 100,000, Sweden 80,000, and various other countries 50,000 tons.

chanically diffused through it in the condition of graphite, the scales of which may be distinctly seen with a magnifying lens, when the surface of a freshly fractured bar is examined. These scales remain unacted upon when the metal is dissolved in dilute acids; the combined carbon under such circumstances unites with hydrogen, and forms an oily looking liquid of ill odour. In addition to carbon, cast-iron also contains silicon, the proportion of which is equally liable to variation; the quantities of silicon which have been found in pig-iron range between 3·5 and 0·25 per cent.

The following table will serve to illustrate the general composition of some varieties of cast-iron :—

	Gay Lussac and Wilson.		Bodemann.	
	Grey Welsh. (coke.)	White iron. (Isère.)	Mottled cold blast	Grey hot blast
			Royal Works, Hartz.	
Carbon { Combined . . . . .	2·45	2·636	2·78	1·44
{ Free . . . . .			1·99	2·71
Silicon . . . . .	1·62	0·260	0·71	3·21
Phosphorus . . . . .	0·78	0·280	1·23	1·22
Manganese . . . . .	traces	2·140	trace	trace
Iron (by loss) . . . . .	95·15	94·684	93·29	91·42
Sulphur . . . . .			trace	trace
Calcium . . . . .			trace	trace
	100·00	100·00	100·00	100·00
* Specific gravity . . . . .			7·43	7·166

In commerce there are three principal varieties of *cast-iron*, known respectively as Nos. 1, 2, and 3. No. 1 is called *grey cast-iron*; No. 2, *mottled cast-iron*; and No. 3, *white cast-iron*. The first two are soft, and contain carbon disseminated in an uncombined form through the mass. Grey cast-iron is soft; it may be filed, drilled, and turned in the lathe, and though somewhat less fusible than the white, is preferred for casting, since when melted its liquidity is more perfect. This variety is that which is generally produced from a furnace in good working order; if cooled suddenly, it is often converted into white cast-iron. The fracture of the mottled variety is in large coarse grains, among which points of graphite are distinctly visible. White cast-iron contains about the same amount of carbon as the mottled-iron, but the whole of the carbon appears to be chemically combined with the metal. The white variety is more fusible than either of the others, is lighter in colour, very hard and brittle, and has a lamellar crystalline fracture.

White cast-iron seems in some cases to owe its colour to the presence of manganese. If white iron be melted, and allowed to cool very gradually, a portion of the carbon crystallizes out as graphite, and grey cast-iron is produced. In the process of casting heavy articles this carbon separates, and is thrown off in the form of brilliant scales, termed by the casters *kish*. The peculiar value of iron for castings depends upon its property of expanding at the moment of solidification. It thus furnishes an admirable material for taking the most minute impressions, as is well exemplified in the beautiful castings obtained from Berlin.

Small articles made of cast-iron, such as key blocks, stirrup irons, &c., may be rendered malleable by packing them in powdered hæmatite, then heating them to redness for some hours, and allowing them to cool very slowly. In this case the oxygen of the oxide removes a portion of the carbon, by a process of cementation the reverse of that which takes place during the manufacture of steel: the carbon is gradually removed from the outer layer of the metal, and is slowly transmitted from particle to particle through the solid bar, till it reaches the surface, where it undergoes oxidation at the expense of part of the oxygen of the hæmatite. The annexed analyses contain the results furnished by a sample of iron both before and after it had been thus treated. The cast-iron was obtained from the Lancashire brown hæmatite:—

	Brittle.	Malleable.
Specific gravity . . .	7.684	7.718
Iron (by loss) . . . .	95.732	98.711
Carbon { combined . .	2.217	0.434
{ uncombined .	0.583	0.446
Silicon . . . . .	0.951	0.409
Aluminum . . . . .	trace	trace
Sulphur . . . . .	0.015	
Phosphorus . . . . .	trace	trace
Sand . . . . .	0.502	
	100.000	100.000

### Conversion of Cast-Iron into Wrought-Iron.

(628) *Refining*.—The pig-iron as delivered from the furnace is, as already noticed, far from pure: it contains variable quantities of carbon, silicon, sulphur, and phosphorus, besides traces of other metals, such as aluminum, calcium, and potassium. Before it can be converted into the wrought-iron of commerce, it has to undergo

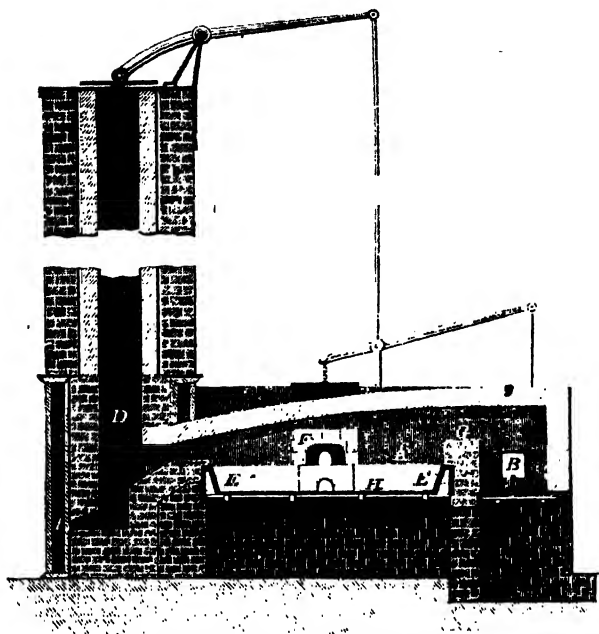
a process for the removal of these extraneous matters. Many castings may be made at once with pig-iron, but it cannot be worked at the forge.

To effect the purification of the crude pig-iron, it is necessary to expose it to the regulated action of oxygen at a high temperature, in order gradually to burn off these oxidizable substances, and leave the iron. The pig-iron is usually first remelted in quantities of from 25 to 30 hundred weight, upon the hearth of a sort of forge, termed the *finery*, or *refinery*; the fire of which is animated by a double row of blast pipes. The metal thus loses from 12 to 16 per cent. of its weight; part of the carbon burns off as carbonic oxide; the silicon becomes converted into silica by the absorption of oxygen, and a portion of the iron forms oxide, which unites with the oxidized silicon, and with the sand which adhered to the surface of the cast metal: a fusible slag consisting of a silicate of protoxide of iron containing a large excess of oxide of iron is thus produced ( $2 \text{FeO}$ ,  $\text{SiO}_2$ ). The excess of oxide of iron in this slag again reacts upon the melted metal, and by imparting a portion of its oxygen to the carbon and silicon disseminated through the mass, burns off an additional quantity of these substances. The melted iron is then run off and formed into a flat cake, 2 or 3 inches thick, and as soon as it begins to solidify it is suddenly cooled by pouring water upon it; a hard, white, brittle mass is thus obtained, which is broken up into fragments. In this operation coke is the combustible generally made use of, but where iron of superior quality is required, as in making tinplate, charcoal is employed. Ordinary coke contains sulphur and earthy impurities which injure the quality of the iron. Portions of sulphur and phosphorus are also separated by oxidation in this process, and accumulate in the slag.

(629) *Puddling*.—The refined metal still retains a considerable proportion of carbon and some silicon. In order to remove them it is next introduced, in charges of from four to five hundred weight, into the *puddling furnace*. This consists of a reverberatory furnace, connected with a chimney of 40 or 50 feet in height, and capable of producing a powerful draught, which is under complete command by means of a damper. Fig. 307, represents a section of the puddling furnace: A, is the bed, or hearth, upon which the iron for puddling is placed; B, is the fire-place with the aperture for stoking, which is closed with coal and not by a door, as usual, in most furnaces; C, is the bridge which separates the fuel from the metal: the hearth, A, is lined with cast-iron plates, E E, which are prevented from melting by the free circula-

tion of air beneath them ; c is the flue leading to the chimney, d, at the top of which the damper is shown ; h is the plate upon

FIG. 307.



which the iron rests during the puddling process ; it is protected from the heat by a coating of slag ; r is the working door of the furnace ; and i is the *flosshole*, or aperture through which the slags are removed from the hearth.

The refined iron is often mixed with a certain proportion of scales of oxide from the forge, and is then gradually brought into complete fusion, carefully avoiding the contact of fuel. The mass is well stirred, so as to incorporate the oxide of iron with the melted metal ; oxygen is transferred from the oxide thus introduced, to the carbon of the melted iron, and carbonic oxide is formed abundantly. An appearance of boiling begins to show itself owing to the escape of the carbonic oxide in jets, which take fire and burn with a blue flame : by degrees the metal becomes less fusible as the carbon diminishes in quantity, and at length it is converted into a granular, sandy mass. The heat is now raised till it becomes very intense, and air is carefully excluded by closing the damper and doors. The metal again begins to soften and agglomerate. The puddler gradually collects it into balls or *blooms* upon the end of an iron rod ; he then removes it from the



furnace in masses of about  $\frac{3}{4}$  of a hundred weight, and subjects it, whilst still intensely hot, to the action either of a massive hammer, or a powerful press, called the *skingling press*. The melted slag is thus forcibly squeezed out, the particles of metal are brought nearer together, and the density is increased. The iron is then fashioned into a bar by passing it between grooved rollers, and the bar thus obtained is cut into lengths, then piled up in a reverberatory furnace and re-heated; it is again rolled, doubled upon itself, and re-heated and rolled. Upon the best qualities of iron this process is repeated several times, in order to render its fibres parallel to each other, by which the toughness of the metal is much increased. The iron is now nearly pure; it contains from  $\frac{1}{1000}$ th to  $\frac{1}{2000}$ th of its weight of carbon, and about  $\frac{1}{1000}$ th of silicon. The presence even of this small proportion of carbon adds materially to the toughness and hardness of the metal. The process of puddling occupies about two hours; and provided it has been properly refined previously, the metal loses 9 or 10 per cent. of its weight.

The slag produced during the operations of puddling and refining consists chiefly of a basic silicate of the protoxide of iron, and contains upwards of 60 per cent. of the metal. This slag or *finery cinder* is reduced in the blast furnace in the same manner as the original ore, but it is always found to produce a defective iron, technically known as *cold short*. Such iron may be forged well at a red heat, but when cold it is brittle and rotten. This defect is attributed to the presence of phosphorus, which is separated from the crude metal in the form of phosphate of iron during the puddling. When the slag is reduced in the blast furnace, both the phosphorus and the iron are deprived of their oxygen, and by their union, as phosphide of iron, form the faulty metal in question.

(630) *Production of Wrought-Iron direct from the Ore.*—The pure ores, which consist of magnetic oxide, or of peroxide of iron, are frequently converted at once into wrought-iron, without the production of cast-iron. This process is practised in the Pyrenees by what is termed the Catalan forge, and still more largely in the *bloomery forges* of the United States. In the American bloomery forge either the hot or the cold blast may be employed:—The ore having been first reduced by stampers to a coarse powder, is placed on the top of the coal in the forge which has been kindled for its reception; a high heap of coal is kept on the fire, and a gradual supply of ore is maintained: as the metal is reduced, it sinks to the bottom in a pasty state; when sufficient has been added

to form a bloom, or ball, the metal is collected on an iron bar, heated before the blast-pipe, and then hammered, rolled, and welded, as if it had come from the puddling furnace (Overman's *Metallurgy*, p. 544). This method yields a very pure iron when charcoal is employed, but the consumption of fuel per ton of metal is much greater than in the blast furnace; a large portion of the ore is also wasted in the form of slags, which are very rich in oxide of iron. The iron produced by this process frequently contains sufficient carbon to give to it some of the properties of steel: for instance, it becomes much harder when heated and suddenly cooled. Iron of this description is valuable in the manufacture of ploughshares, and heavy articles requiring both toughness and hardness.

### *Manufacture of Steel.*

(631) Iron, when combined with a smaller proportion of carbon than is contained in cast-iron, furnishes the valuable compound well known as *steel*, of which there are several varieties. The quantity of carbon in good steel varies between 0.7 and 1.7 per cent., but steel which possesses the greatest tenacity has been found to contain from 1.3 to 1.5 per cent. of carbon, and about 0.1 of silicon. *Natural steel* is produced directly from the best cast-iron by heating it by means of charcoal on the refining hearth as in the operation which precedes the process of puddling; the oxygen burns off a portion of the carbon from the cast-iron, and steel remains. The preparation of natural steel is, therefore, an intermediate stage in the conversion of cast into wrought-iron. The mass thus obtained is rendered homogeneous by forging. It yields a steel of inferior quality, which is employed for making agricultural implements and springs for machinery.

For more delicate purposes *blistered steel* is made use of: this is obtained by means of *cementation*, which is an operation just the reverse of that by which natural steel is formed. This process is carried on in a furnace containing one or more rectangular boxes of brickwork or stoneware for the reception of the bars of iron which are to be converted into steel. This conversion is effected by heating the iron in contact with charcoal, which is usually mixed with about a tenth of its weight of common salt and wood ashes, forming what is technically termed *cement powder*. In preparing a charge, the bottom of the boxes is covered with a layer of the cement powder to the depth of about an inch, and upon this, at intervals of about half an inch, a layer of bars of the

best malleable iron is placed. The interstices between the bars are also filled with cement powder, which is tightly packed around the iron; above this is a layer of the powder, then another layer of bars, and so on in succession until the box is nearly full. The remaining space is now covered with a layer of damp sand about three inches in depth, and the fire is gradually raised to a full red heat, or about the temperature required for melting copper; at this point it is steadily maintained. One of the bars of steel is so placed that it can be removed from time to time during the operation for the purpose of ascertaining the process of the carburization by inspection. The process is usually complete in six or eight days; but the time required necessarily varies with the thickness of the iron bars operated on. The steel thus obtained retains the form of the iron, but it is covered with blebs or blisters, by which the surface is rendered irregular and uneven. The mass is found to have been penetrated by carbon which has been transferred from particle to particle of the metal, the properties of which it has completely changed. It has been supposed that these blisters may possibly arise from the combination of parts of the carbon with oxygen derived from particles of oxide of iron, which are apt to be mechanically retained even in the most carefully prepared bars. Carbonic oxide would thus be produced, and imprisoned in the tenacious metal, which in its softened state would be raised by it into bubbles or blebs. Great care, however, is generally taken to exclude slag and oxide of iron from bars which it is intended to convert into steel: in the majority of instances it is more probable, as suggested by Mr. T. H. Henry, that the blisters are occasioned by the combination of carbon with the sulphur which is still retained by the iron, and which, by forming the volatile bisulphide of carbon, would produce the effect. All bar iron contains traces of sulphur; but in steel sulphur is never present, and there appears to be no other mode of accounting for its uniform absence than its removal during the process of carburization in the form of bisulphide of carbon.

By the process of cementation the iron has been combined with about 1.5 per cent. of carbon: it is now much more fusible than before. It has also entirely lost its fibrous texture; and when broken across exhibits a close, fine-grained fracture. Steel may also be made without direct contact with carbon by simply heating the bars in carburetted hydrogen. This process is more rapid and the results are more uniform than those obtained by cementation.

Blistered steel is never homogeneous, the surface being always more highly carburetted than the inner portions of the bars. This variety of steel is employed for files, tools, and hardware of all descriptions. When blistered steel is fused it forms *cast-steel*, which, from being more uniform in texture, is of superior quality, as the carbon is more equally distributed throughout the mass: it is employed for cutlery of the best description. *Tilted-steel* is also obtained from blistered steel; it is first broken up into lengths of about 18 inches, then bound into faggots and raised to a welding heat in a wind furnace, where it is covered with sand, which combines with the oxide of iron and forms a fusible slag: the red-hot faggot is then rolled, and forged, by means of the tilt-hammer, into smaller bars. All steel is improved by this process of hammering. These tilted bars, when broken up and welded together, form *shear-steel*. For many purposes the addition of a small quantity of manganese is an improvement to the quality of the steel. If about 1 per cent. of carbide of manganese, or of a mixture of charcoal and oxide of manganese be introduced into the melting-pot, a steel is obtained of fine, close grain, which admits of being welded to wrought-iron; a property not possessed by ordinary steel. The experiments of Faraday and Stodart led them to the conclusion that the addition of small quantities of silver, of chromium, or of rhodium, to good steel, furnished a steel of a superior kind. According to Mr. Brande, when steel is to be used for the manufacture of dies for coining, the presence of a small proportion of phosphorus is beneficial. When dilute nitric acid falls upon steel, a dark grey spot is produced, owing to the solution of the metal in the acid whilst its carbon remains unacted upon: upon iron the acid produces a green spot. The acid acts unequally upon different parts of the surface, in certain of the finer varieties of steel, and thus produces a veined appearance, such as was formerly given to the celebrated Damascus blades. According to M. Bréant, the Damascus steel is more highly carburetted than ordinary steel, and if allowed to cool slowly, it separates into layers of two different degrees of carburation; hence certain parts, when acted on by dilute acid, leave more carbon than others; the form and direction of these veins vary with the mode of forging adopted.

*Wootz* is a finely damasked, hard steel, of excellent quality, which is obtained from India. Mr. Faraday found aluminum in a sample of this steel which he analysed, and was disposed to refer its peculiar qualities to the presence of this metal. It

appears, however, from the experiments of Mr. Henry (*Phil. Mag.* July, 1852), that aluminum is not always present in wootz. He gives the following as the composition of a bar of genuine Indian wootz, of specific gravity 7·727 :—

Carbon	{ combined . . . . .	1·340
	{ uncombined . . . . .	0·312
Silicon	. . . . .	0·045
Sulphur	. . . . .	0·181
Arsenic	. . . . .	0·037
Iron	. . . . .	98·092
		<hr/>
		100·000

Other analysts have also failed in finding aluminum in wootz.

The physical properties of steel differ materially from those of iron. As already mentioned, it becomes granular in texture, brittle, and more easily melted. Its most characteristic property, however, consists in its power of assuming a hardness scarcely inferior to that of the diamond when heated to redness and then suddenly cooled by plunging it into water, mercury, or oil. After this treatment it is rendered extremely brittle, and almost perfectly elastic.

This extreme hardness and brittleness may be removed by the process of *tempering*, which is a peculiar mode of annealing; it consists in heating the steel moderately and then allowing it to cool slowly. The tempering of steel is an operation of great practical importance, as from the variety of purposes to which steel is applied, it is required of very different degrees of hardness, and upon the due adjustment of this quality much of its utility depends. The degree to which the temperature is raised in the second heating regulates this point: the higher the heat the softer is the steel. In practice the workman judges with sufficient accuracy of the temperature to which the metal has been exposed, by observing the colour which the steel assumes, owing to the varying thickness of the film of oxide which forms upon its surface. It is easy to show that this colour is due to the formation of a film of oxide; for by painting on the surface of the steel various devices in oil or varnish, and then exposing it to heat, the surface of the blade becomes coloured in every part excepting those portions which have been varnished, and these, when the varnish is removed, retain their original polish. The first perceptible tint is a light straw colour, which is produced by the lowest degree of heat, and indicates the hardest temper; the heat required is from 430° to 450°; it is used for lancets, razors, and surgical instruments: at 470° a

full yellow is produced; it is the temper fitted for scalpels, pen-knives, and fine cutlery. The temperature of  $490^{\circ}$  gives a brown-yellow, which is the temper for shears intended for cutting iron. At  $510^{\circ}$  the first tinge of purple shows itself: this is the temper employed for pocket-knives:  $520^{\circ}$  gives a purple, which is the tint for table and carving knives. A temperature from  $530^{\circ}$  to  $570^{\circ}$  produces various shades of blue, such as are used for watch springs, sword blades, saws, and instruments requiring great elasticity (Stodart). The different degrees of heat may be exactly regulated by heating the different articles in a fusible metal or oil bath, the temperature of which is ascertained by means of thermometers, though in ordinary cases this degree of nicety is not observed.

Hardened steel is somewhat less dense than wrought steel. It appears that a portion of the carbon contained in steel, before the alloy has been hardened, is in the uncombined state; this portion is left in the form of graphitic scales, when the metal is dissolved in hydrochloric acid: but after the steel has been hardened, the whole of the carbon is chemically united with the iron; and when treated with acids, is left in the form of a liquid hydrocarbon. Before it has been hardened it may be worked as easily as iron, and in certain cases may be welded upon that metal. Instruments are completely finished in the soft state, and are then hardened and subsequently tempered.

It is sometimes desirable to convert articles manufactured from soft iron superficially into steel. This is termed *case-hardening*, and is effected by heating them in contact with powdered cast-iron turnings, or sometimes with powdered charcoal. The same object is attained if they are sprinkled when red-hot with powdered ferrocyanide of potassium.

(632) In order to obtain iron chemically pure, Berzelius recommends that filings of the best bar iron be intimately mixed with one-fifth of their weight of pure peroxide of iron, and placed in a Hessian crucible, covered with pounded glass (free from lead); the cover is then to be carefully luted on, and the crucible to be exposed for an hour to the strongest heat of a smith's forge. By this means all traces of carbon and of silicon are oxidized at the expense of the oxygen of the peroxide of iron. If the operation be successful, the iron will be melted into a button, with a lustre approaching that of silver. Such iron is very tough, and much softer than ordinary bar iron; it has a sp. gr. of 7.8439. Pure iron may also be obtained in the state of fine powder, by decomposing the pure peroxide at a red heat in a current of hydrogen gas.

(633) *Properties of Bar Iron.*—The bar iron of commerce is never pure. It always retains small quantities of carbon, varying from 0.2 to 0.4 per cent., and traces of silicon and sulphur; occasionally, also of phosphorus and arsenic. The presence of this small quantity of carbon much increases its hardness and tenacity, but the other ingredients act injuriously upon the metal.

Bar iron has a bluish white or grey colour, and is endowed with considerable lustre and hardness; it takes a high polish: its texture is usually fibrous, and when broken across, it exhibits a ragged or hackly fracture; when rubbed, it emits a peculiar characteristic odour. The average specific gravity of good bar iron is 7.7. It requires the most intense heat of a wind furnace for its fusion. Iron passes through a soft pasty condition before it is completely melted; this property is one of great practical importance: if two pieces of iron be heated to whiteness, sprinkled with sand, and hammered together, they may be united or *welded* so completely that the junction is as tough as any other part of the metal. The sand is used as a flux to the oxide of iron, with which it forms a slag, which coats each piece of the metal; by the blow of the hammer this layer of melted matter is forced out, and the two clean surfaces of metal unite together. At a red heat iron may be forged into any shape with facility, but at ordinary temperatures it possesses but little malleability, as compared with gold and silver. It however admits of being rolled into very thin sheets. In ductility iron is unsurpassed, and in tenacity it far exceeds all other known substances.

If compared with other metals, iron is inferior to many of them as a conductor of heat and of electricity. Its susceptibility to magnetism is peculiar; no metal exhibiting this property in any marked degree, excepting cobalt and nickel, and in them the power is developed to a much smaller extent. But though iron in its pure state is susceptible of magnetic induction, it cannot be permanently magnetized unless it be combined with carbon, as in steel; with oxygen, as in the loadstone ( $\text{Fe}_3\text{O}_4$ ); or with sulphur, as in certain varieties of pyrites ( $\text{Fe}_3\text{S}_4$ ), and ( $\text{Fe}_7\text{S}_8$ ). It is especially worthy of observation, that if oxygen or sulphur be present in quantity either greater or less than in these particular compounds, the power of retaining magnetism is destroyed, and the mass becomes almost indifferent to the action of a magnet. Iron loses its magnetic power when heated to redness, but recovers it again on cooling.

At a high temperature iron burns readily, emitting vivid scintillations, as may be seen at the blacksmith's forge, or still more brilliantly when a glowing wire is introduced into a jar of oxygen.

It preserves its lustre unchanged in dry air at ordinary temperatures, but when exposed to a moist atmosphere, its surface is quickly altered, and it becomes covered with rust. When once a spot of rust begins to show itself, the oxidation proceeds rapidly; moisture is absorbed from the air by the oxide, and thus a species of voltaic action is produced, the oxide performing the part of an electro-negative element, whilst the iron becomes electro-positive, and the atmospheric moisture acts as the exciting liquid. The carbonic acid of the air contributes in an important way towards producing this change: protocarbonate of iron is first formed, and afterwards it passes into the hydrated oxide, or rust of iron: this rust always contains ammonia, derived from the reaction of the hydrogen of the water upon the nitrogen of the atmosphere. Even the native oxides of iron invariably contain traces of ammonia (Chevallier). Iron may be kept for any length of time without undergoing any change in water quite free from air, as well as in water containing a little free alkali. In a very finely divided state, such as that produced by reducing precipitated oxide of iron at a low temperature in a current of hydrogen gas, the metal takes fire by mere exposure to the atmosphere. If a small quantity of alumina be precipitated with the oxide of iron so as to interpose some foreign matter between the particles of the metal, this pyrophoric property is much increased. At a red heat iron rapidly decomposes water, and liberates hydrogen (293), whilst the iron is converted into minute crystals of the black or magnetic oxide; the following equation illustrates the chemical change:  $4 \text{H}_2\text{O} + 3 \text{Fe} = 4 \text{H} + (\text{FeO}, \text{Fe}_2\text{O}_3)$ .

Iron is soluble in diluted sulphuric and hydrochloric acids, with extrication of hydrogen. Even carbonic acid, when contained in water from which air is excluded, slowly dissolves this metal with extrication of hydrogen, and the carbonate of iron is dissolved in the excess of carbonic acid. It is rapidly attacked by nitric acid, with abundant evolution of binoxide of nitrogen.

(634) *Passive Condition of Iron.*—Under certain circumstances iron may be kept in concentrated nitric acid for weeks, without the slightest action, or alteration of the polish of its surface. There are various methods of producing this *passive condition* of iron in an acid of a moderate degree of concentration; some of these seem to indicate an intimate connexion with its voltaic relations. This will be rendered evident from the following statement of some of the circumstances under which this remarkable phenomenon is manifested. If a piece of clean iron wire be introduced into nitric acid, of a sp. gr. of about 1.35, immediate and brisk



action ensues; but if the metal be touched beneath the surface of the liquid with a piece of gold, of platinum, or of plumbago, the chemical action is suddenly arrested if the temperature of the acid has not been allowed to rise too high. If a second iron wire be made to touch the first, and then be introduced into the acid, it also is rendered inactive. This second wire may be used in like manner to render a third inactive. But if any of these inactive wires be withdrawn from the acid, and exposed to the air for a few seconds, it will be found to be rapidly acted on upon again introducing it into the acid.

By heating the end of a clean iron wire in the flame of a spirit lamp so as to give it a superficial coating of oxide, the wire is brought into the passive condition.\* If into acid containing a passive wire, a second ordinary wire, not in contact with the first, be introduced, brisk action on the ordinary wire ensues; and on causing the passive wire to touch the active one, immediate action occurs on both.

Strong nitric acid, of sp. gr. 1.45, renders all iron passive; the metal may be kept in it for years without losing its brilliancy, or showing any action; and a wire withdrawn from the strong acid, and plunged into acid of 1.35, still remains passive. If it be wiped first and then plunged into the weaker acid, it immediately begins to be dissolved. If the acid be diluted below a density of 1.35, it rapidly dissolves the metal, whatever may have been its previous condition.

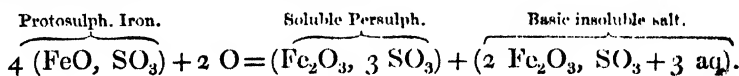
(634 bis) Iron forms alloys with most of the metals; but they are not in general of much importance. The presence of small quantities of copper, arsenic, or sulphur in iron, is said to occasion a defective quality of metal, technically known as *red short*. Such iron is tough at ordinary temperatures, but becomes brittle when heated to redness for forging.

The mode of preparing zinc-plate, or galvanized iron, has been already described (591). Tin plate is prepared by an analogous process; it consists of iron superficially alloyed with tin. The object of the employment of zinc and tin in this manner is to protect the iron from rust, and to enable the workman readily to solder the joints of vessels made of these materials.

\* M. Nicklès finds that similar effects are produced with wires of cobalt or of nickel, though with them the action is less strongly marked. Such wires, if placed in voltaic relation with an active wire of the same metal, are found to be strongly electro-negative towards it; but passive iron, cobalt, and nickel, are electro-positive in relation to platinum. Dr. Andrews has shown that bismuth also may be rendered passive in concentrated nitric acid.

(635) COMPOUNDS OF IRON WITH OXYGEN.—Iron yields four definite compounds with oxygen: 1. The *protoxide* ( $\text{FeO}$ ), which is the basis of the green salts of iron: 2. The *sesquioxide* ( $\text{Fe}_2\text{O}_3$ ), which is the base of the red salts: 3. The black or *magnetic oxide*, which may be viewed as a compound of the two preceding oxides ( $\text{Fe}_3\text{O}_4$ ) or ( $\text{FeO}, \text{Fe}_2\text{O}_3$ ); it does not form any definite salts: 4. *Ferric acid* ( $\text{FeO}_3$ ) which is a weak and unstable metallic acid, and as such combines with the alkalis.

*Protoxide of Iron* ( $\text{FeO}$ ) *Eq. 36.*—It is obtained in the form of a white hydrate by dissolving a pure protosalt of iron in water recently boiled, and precipitating by an alkali. If boiled in a vessel from which air is excluded, it loses its water of hydration like the oxide of copper under similar circumstances. The hydrated oxide absorbs oxygen greedily from the air, passing through various shades of light green, bluish green, and black, till finally it assumes an ochry hue, due to the formation of the sesquioxide. It is insoluble in water, but is somewhat soluble in ammonia; this solution quickly absorbs oxygen from the air, and a film of insoluble sesquioxide of iron is formed. It is readily dissolved by acids, and forms with them salts which have a green colour, and a styptic, inky taste. The solutions of these salts by exposure to the air are all decomposed by absorbing oxygen; in which case salts of the sesquioxide are formed, one portion of which is retained in solution, whilst a basic salt of the sesquioxide falls as a rusty insoluble precipitate. For example, in the case of the protosulphate of iron, 4 equivalents of the salt by absorbing 2 equivalents of oxygen are decomposed as follows:



(636) *Sesquioxide of Iron* ( $\text{Fe}_2\text{O}_3$ ).—The anhydrous sesquioxide is obtained for the arts by igniting the protosulphate of iron, and is known under the names of *colcothar*, *crocus of Mars*, or *rouge*, according to the degree of levigation to which it has been submitted; it is extensively employed, amongst other uses, for polishing glass, and by jewellers for putting a finish to their goods. It is also employed as a red pigment.

The sesquioxide occurs native in great abundance: several of its varieties have been already mentioned as among the most valuable ores of iron. The specular ore of Elba often presents natural facets of the most perfect polish, and of remarkable size and lustre. The specific gravity of this oxide is 5.22. It occurs

in forms of the rhombohedral system, and is isomorphous with alumina in corundum. Red hæmatite or bloodstone, another of its varieties, is extremely hard, and when polished, is employed for burnishing gilt trinkets.

Brown hæmatite is the hydrate ( $2 \text{Fe}_2\text{O}_3, 3 \text{aq}$ ) *Sp. Gr.* 3.98. This mineral is readily dissolved by acids. Another native hydrate ( $\text{HO}, \text{Fe}_2\text{O}_3$ ) has been found crystallized in cubes; it is isomorphous with the magnetic oxide of iron ( $\text{FeO}, \text{Fe}_2\text{O}_3$ ), to which it corresponds in composition, 1 equivalent of protoxide of iron being displaced by 1 equivalent of water. Brown hæmatite gives the red and yellow colour to the different varieties of clay.

The sesquioxide is best obtained in a state of purity, by precipitating the sesquichloride of iron by ammonia in excess. It falls as a bulky light brown flocculent hydrate, which shrinks remarkably as it dries. This hydrate retains a little ammonia which is easily expelled by heat. If dried at a dull red heat the mass glows brightly as it parts with the last portions of water, and after this, it is dissolved by acids with difficulty: at a very high temperature the sesquioxide loses  $\frac{1}{3}$  of its oxygen, and is converted into the magnetic oxide of iron.

In its hydrated state sesquioxide of iron is easily soluble in acids, forming salts which do not crystallize; many of them are deliquescent, and have a strong inky taste. Their concentrated solutions have the property of dissolving a considerable excess of oxide, in which case they assume a deep red colour. If these basic solutions be diluted and boiled, the peroxide of iron is entirely separated in the form of an insoluble subsalt.

Hydrated sesquioxide of iron is now used to some extent for the purpose of purifying coal gas from sulphuretted hydrogen, which is always produced during the distillation of coal. For this purpose the oxide is mixed with sawdust, and placed in layers of two or three inches in thickness, upon the perforated shelves of a dry lime purifier: protosulphide of iron, water, and free sulphur are formed;  $\text{Fe}_2\text{O}_3 + 3 \text{HS} = 2 \text{FeS} + 3 \text{HO} + \text{S}$ . After the mixture has ceased to absorb any more sulphuretted hydrogen, it is oxidized by exposure to a current of air, sesquioxide of iron is thus reproduced, and sulphur is set free;  $2 \text{FeS} + 3 \text{O} = \text{Fe}_2\text{O}_3 + 2 \text{S}$ . The mixture may again be used for the same purpose as at first, and this process may be repeated several times in succession, until the accumulation of sulphur mechanically impairs the absorbent powers of the mixture. Considerable elevation of temperature attends the act of reoxidation, which must therefore be prevented from taking place with too much rapidity.

Sesquioxide of iron combines with some of the more powerful bases, towards which it acts the part of a feeble acid. The compounds which it forms by heating it with potash and soda are easily decomposed by water. According to Pelouze, when 4 equivalents of lime and 1 equivalent of peroxide of iron are precipitated together and boiled, they unite and form a white compound ( $4 \text{ CaO}, \text{Fe}_2\text{O}_3$ ) which is readily decomposed by the feeblest acids. Sesquioxide of iron occurs native combined with oxide of zinc in crystals, mixed with oxide of manganese, constituting *Franklinite*. With protoxide of iron it forms the black or magnetic oxide of iron.

(637) *Black or Magnetic Oxide of Iron* ( $\text{FeO}, \text{Fe}_2\text{O}_3$ ), *Eq.* 116; *Sp. Gr.* 5.09.—This oxide occurs as a well-known mineral, the *loadstone*, which acquires its magnetism from the inductive influence of the earth. It is found in primitive rocks, forming beds, or sometimes as in Sweden, entire mountains. It furnishes a very pure and excellent iron, of which a large quantity is annually supplied from the Swedish and American mines. It has a black colour and metallic lustre; it crystallizes in cubes, octohedra, or rhombic dodecahedra. Magnetic oxide of iron is the principal constituent of the scales of oxide which are detached during the forging of wrought-iron. It fuses at a high temperature, and is formed when iron is burned in oxygen; the sesquioxide which is the result of the action losing part of its oxygen, owing to the intensity of the heat developed during the combustion. The same compound is formed by passing steam over heated iron turnings. A hydrate of this oxide may be procured by dissolving equal weights of sulphate of the protoxide of iron in separate portions of water, and boiling one of these with nitric acid, which is gradually added to the boiling liquid until it ceases to evolve binoxide of nitrogen: when this point is reached, the whole of the protoxide of iron will have been converted into peroxide: the two portions of the solution are then mixed together and precipitated by carbonate of soda, which is added in slight excess: the solution and precipitate are boiled together, and the black oxide falls as a heavy crystalline powder. The magnetic oxide is soluble without difficulty in hydrochloric acid, as well as in nitric acid and aqua regia; this oxide however does not form specific salts, but mixtures of salts of the protoxide and peroxide.

(638) *Ferric Acid* ( $\text{FeO}_3$ ) *Eq.* 52.—If a mixture of 1 part of sesquioxide of iron and 4 of nitre be heated to full redness for some time, a brown mass is obtained, which with water gives a beautiful violet coloured solution, due to the presence of ferrate of

potash. In this compound the iron is combined with a larger quantity of oxygen than in the sesquioxide, but the ferric acid has not been obtained in an insulated form. Ferrate of potash may be more easily procured by suspending 1 part of recently precipitated peroxide of iron in a concentrated solution of potash consisting of 30 parts of hydrate of potash and 50 of water, and then transmitting a current of chlorine gas: the ferrate of potash is insoluble in a concentrated solution of potash, and is deposited as a black powder which may be drained upon a tile (Fremy). This compound is very soluble in water, but is precipitated in black flocculi by a large excess of alkali. It is a very unstable salt: in dilute solutions the alkali becomes free, hydrated sesquioxide of iron subsides, and oxygen escapes. Organic matter decomposes it speedily, just as it does the permanganate of potash: a temperature of  $212^{\circ}$  destroys it instantly if in solution, and the addition of an acid, even in quantity insufficient to neutralize the whole of the alkali, causes the immediate separation of oxygen, and precipitation of the sesquioxide of iron.

Ferrates of baryta, strontia, and lime may be obtained in the form of red insoluble precipitates, by admixture of solutions of the salts of the earths with a solution of the ferrate of potash.

(639) COMPOUNDS OF IRON WITH SULPHUR.—Sulphur combines with iron in several proportions: the protosulphide  $\text{FeS}$ , and the bisulphide  $\text{FeS}_2$ , are the most important; but besides these, a sesquisulphide  $\text{Fe}_2\text{S}_3$ , may be formed by precipitating the persalts of iron by an alkaline sulphide; and two magnetic sulphides of iron ( $6 \text{ FeS}$ ,  $\text{FeS}_2$ ) and ( $2 \text{ FeS}$ ,  $\text{FeS}_2$ ) are found native.

*Protosulphide of Iron* ( $\text{FeS}$ ), *Eq.* 44, may be prepared by heating a bar of iron to whiteness and bringing it into contact with a roll of sulphur: immediate union takes place, the resulting sulphide melts and runs down in drops. When formed in this manner it usually contains an excess of sulphur. Protosulphide of iron dissolves both iron and sulphur if either be present in excess; its composition therefore is variable. Like carbon, the presence even of a very minute portion of sulphur alters the quality of wrought-iron, which if it contain even  $\frac{1}{10000}$  of sulphur, is rendered 'hot short.' Anhydrous protosulphide of iron has a reddish brown colour; it is dissolved by dilute sulphuric or hydrochloric acid with evolution of sulphuretted hydrogen: this decomposition is frequently employed in the laboratory as a convenient source of sulphuretted hydrogen. Nitric acid and aqua regia decompose it and form pernitrate or perchloride of iron, setting part of the sul-

phur free, and converting the residue into sulphuric acid. When heated in the open air, this sulphide absorbs oxygen and becomes converted into sulphate of iron; at a still higher temperature it is decomposed, sulphurous and sulphuric acids escape, and sesquioxide of iron remains.

• Protosulphide of iron may be obtained in combination with water, as a black hydrate, by precipitating a solution of a protosalt of iron with one of an alkaline protosulphide; in this condition it rapidly attracts oxygen from the air, and assumes a brownish red colour, sesquioxide of iron being formed and sulphur liberated. The hydrated protosulphide of iron is slightly soluble in the alkaline sulphides, with which it forms green solutions.

If iron filings be mixed with two-thirds of their weight of sulphur in powder, and moistened, the mixture becomes hot when exposed to the air, and absorbs oxygen with sufficient rapidity to cause it in many cases to inflame; sulphide of iron is at first formed, which quickly becomes converted into sulphate. A valuable lute for the joints of iron vessels is composed of a mixture of 60 parts of iron filings sifted fine, and 2 of sal ammoniac in fine powder intimately blended with 1 part of flowers of sulphur. This powder is made into a paste with water and applied immediately; in a few minutes it becomes hot, swells, disengages sulphuretted hydrogen, and soon sets as hard as iron itself.

(640) *Bisulphide of Iron* ( $\text{FeS}_2$ ), *Eq.* 60, *Sp. Gr.* 4.98.—This compound is found abundantly in the native state, constituting the *iron pyrites* of mineralogists. It occurs in the strata of every period: when found in the older formations it is crystallized in cubes of a brassy lustre, and is hard enough to strike fire with steel; but in the tertiary strata it more frequently occurs in fibrous radiated nodules. The formation of iron pyrites may occasionally be traced to the slow deoxidation of sulphates by organic matter in waters containing carbonate or other salts of iron in solution; it is then frequently deposited in cubes or octohedra. This appears to be the usual mode of its formation in alluvial soils. Some varieties of iron pyrites, especially those found in the tertiary strata, are speedily decomposed by exposure to air; oxygen is absorbed, and protosulphate of iron formed. This decomposition occurs with greater facility if the sulphide be mixed with other substances, as is the case in the aluminous schists; in which by the further action of air, a subsulphate of the peroxide of iron is formed, whilst the liberated sulphuric acid reacts upon the alumina, magnesia, or lime of the soil, and forms

sulphates; those of alumina and magnesia may be extracted by lixiviation. The ordinary crystallized pyrites from the older strata is not thus decomposed; but a variety of a whiter colour is rapidly disintegrated by exposure to the weather; this form of pyrites is known as *white iron pyrites*; it crystallizes in right rhomboidal prisms, but it possesses the same chemical composition as the yellow cubes.

Pyrites is not acted upon by sulphuric or hydrochloric acid, but it is rapidly oxidized and dissolved by nitric acid and by aqua regia. When heated in close vessels it fuses, and sulphur is expelled. If heated in the air it burns with flame, peroxide of iron is formed, whilst sulphurous acid escapes in large quantity. This circumstance has been turned to account in the manufacture of oil of vitriol, for which purpose enormous quantities of *mundic*, as the bisulphide is termed by the workmen, are annually consumed. Iron pyrites may be artificially prepared by exposing a mixture of powdered protosulphide of iron with half its weight of flowers of sulphur, in a covered crucible, to a heat below redness, as long as sulphurous fumes escape.

(641) *Magnetic Sulphide of Iron* ( $6 \text{ FeS} + \text{FeS}_2$ ), *Sp. Gr.* 4.65. —This compound exhibits a brassy lustre, but is distinguished from ordinary pyrites by its solubility in hydrochloric acid. It is often formed when sulphur and iron are heated together in preparing the protosulphide for use in the laboratory. Another variety of magnetic pyrites consists of ( $2 \text{ FeS} + \text{FeS}_2$ ).

*Mispickel*, or arsenical pyrites, is an arsenio-sulphide of iron ( $\text{FeS}_2 + \text{FeAs}$ ) which, amongst other localities, occurs abundantly in the Harz, in Saxony, and in some of the Cornish mines; it crystallizes in right rhombic prisms, of a steel-grey colour and metallic lustre. When heated in close vessels it is partially decomposed, and sulphide of arsenic sublimes. If exposed to a high temperature in the open air it produces sesquioxide of iron, whilst arsenious and sulphurous acids escape. Analogous compounds of cobalt and nickel occur amongst the ores of these metals.

*Subphosphide of Iron* ( $\text{Fe}_4\text{P}$ ) may be obtained by reducing the phosphate of the metal with charcoal: it fuses at a red heat, and forms an extremely hard, brittle mass, which dissolves both phosphorus and iron in all proportions.

(642) **COMPOUNDS OF IRON WITH CHLORINE.**—Iron forms with chlorine two compounds, a protochloride,  $\text{FeCl}$ , and a sesquichloride,  $\text{Fe}_2\text{Cl}_3$ , which correspond in composition to the salifiable oxides of the metal.

*Protochloride of Iron* ( $\text{FeCl}$ ); *Eq.* 63.5.—By passing dry hydrochloric acid gas over ignited metallic iron, the acid is decomposed, hydrogen gas escapes, chlorine combines with the iron, and a white anhydrous protochloride of the metal sublimes at a temperature at which glass begins to soften. Its solution may be formed by dissolving iron in hydrochloric acid; the hot, saturated liquid deposits the salt on cooling in green crystals, which contain 4 equivalents of water of crystallization. It is very soluble in water, and is taken up in considerable quantity by alcohol. If heated in the open air chlorine escapes and peroxide of iron remains.

Protochloride of iron unites with chloride of ammonium and forms a double salt, from which the iron may be deposited upon various metallic articles, by boiling them in this solution with scraps of zinc; the zinc displaces the iron, which is deposited in a coherent lamina upon the other metals in consequence of a voltaic action.

*Sesquichloride of Iron* ( $\text{Fe}_2\text{Cl}_3$ ); *Eq.* 162.5.—This compound sublimes in anhydrous brown scales when dry. Chlorine gas is transmitted over iron heated to redness. The anhydrous chloride is very deliquescent, and hisses when thrown into water, forming a red solution. It is also soluble both in alcohol and ether. In a hydrated condition it may be procured by evaporating a solution of the protochloride through which chlorine has been passed to saturation, or by dissolving hydrated peroxide of iron in hydrochloric acid: the solution, by concentration, yields large, red, deliquescent crystals ( $\text{Fe}_2\text{Cl}_3, 6 \text{ aq}$ ), but the salt cannot be rendered anhydrous by evaporation, as it is decomposed into hydrochloric acid and peroxide of iron. Perchloride of iron forms a double salt with chloride of ammonium, which crystallizes readily in cubes, and is known in pharmacy as the *ammonio-chloride of iron*. The composition of this salt varies considerably: it is of a ruby-red colour, and seldom contains more than 2 per cent. of iron.

An *oxychloride of iron* is formed when a solution of the protochloride of the metal is exposed to the air, or when the perchloride is precipitated by a small quantity of caustic alkali. It is insoluble in water containing salts, but is partially soluble in pure water.

The *iodides* and *bromides* of iron correspond in composition to the chlorides.

*Protiodide of Iron* ( $\text{FeI}$ , *Eq.* 155), is formed by digesting iron wire or filings, in a closed vessel, with four times their weight of iodine suspended in water; direct combination between the elements



takes place, the iodide is dissolved and forms a pale green solution, which, by evaporation in vacuo, yields crystals containing 4 equivalents of water. By a continued heat they may be rendered anhydrous, and in that state are fusible. By exposure to air, the solution absorbs oxygen and is decomposed; iodine is set free, and an oxyiodide of iron falls. This change is retarded by mixing the solution with strong syrup; and as the compound is employed in medicine, this method is adopted to preserve uniformity in its composition. A *sesqui-iodide* may be formed by treating iron with an excess of iodine.

(643) *Protosulphate of Iron, Copperas, or Green Vitriol*, ( $\text{FeO}$ ,  $\text{SO}_3$ , 7 aq): *Eq.* 75 + 63: *Sp. Gr. crist.*, 1.857, *anhydrous*, 3.138.—This salt is prepared in a state of purity by dissolving 1 part of pure iron, or  $1\frac{1}{2}$  of its protosulphide by the aid of heat, in  $1\frac{1}{2}$  parts of oil of vitriol diluted with 4 of water. On filtering the solution quickly, it deposits beautiful transparent, bluish-green, rhomboidal crystals on cooling, which contain 7 equivalents of water of crystallization. They effloresce in a dry air, and form a white crust, which soon becomes of a rusty brown colour, owing to the absorption of oxygen and formation of a sub-sulphate of the peroxide. If crystallized at a temperature of  $176^\circ \text{F}$ . the protosulphate forms right rhombic prisms, which contain only 4 equivalents of water. It may also be obtained crystallized with 3 and with 2 equivalents of water. For commercial purposes sulphate of iron is formed by the decomposition of iron pyrites, or of aluminous schists containing pyrites, as already described when speaking of the manufacture of alum. The sulphate of iron thus obtained has a grass-green colour, owing to the presence of persulphate of iron. Sulphate of iron is largely used in combination with astringent vegetable matters as a black dye; ordinary writing ink is a compound of this kind.

This salt is insoluble in alcohol, and requires twice its weight of cold water for its solution. If exposed to the air, the solution absorbs oxygen, and a rusty precipitate occurs, which is a basic persulphate composed of  $2\text{Fe}_2\text{O}_3$ ,  $\text{SO}_3$ , 3 aq, while persulphate of iron remains in solution. If heated gradually, the protosulphate loses 6 equivalents of its water of crystallization and forms a white powder; 1 equivalent of water is retained at all temperatures below  $500^\circ$ . At a red heat the sulphate is decomposed; a portion of the acid yields one-third of its oxygen to the protoxide of iron, which is converted into the peroxide, whilst sulphurous acid escapes; the remainder of the acid distils in the anhydrous form;  $2(\text{FeO}, \text{SO}_3) = \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$ ; but as in practice the salt cannot

be rendered anhydrous in large quantities, a little water distils with the sulphuric acid, which is condensed as a brown fuming liquid, the 'Nordhausen sulphuric acid' (346). The residual oxide of iron is sold under the name of colcothar.

The aqueous solution of protosulphate of iron, in common with that of all the protosalts of this metal, absorbs a large quantity of binoxide of nitrogen, forming a deep brown solution, which has a powerful affinity for oxygen; if this solution be heated in close vessels the gas is for the most part expelled unchanged; if heated in air, nitric acid is formed in the liquid, and this converts the iron into a salt of the peroxide.

With the sulphates of potash and ammonia, green vitriol forms salts precisely analogous in form and composition to those which are formed by these sulphates with sulphate of copper. The formula of the potash salt is  $\text{FeO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6 \text{ aq.}$

*Persulphate of Iron* ( $\text{Fe}_2\text{O}_3, 3 \text{ SO}_3$ , Eq. 200), is made either by treating brown hæmatite with an excess of strong sulphuric acid, allowing it to digest for some time and then expelling the excess of acid at a heat short of redness; or by adding to the solution of 1 equivalent of protosulphate of iron,  $\frac{1}{2}$  an equivalent of oil of vitriol, boiling, and adding to the solution nitric acid in small quantities as long as any red fumes are given off. A yellowish-white deliquescent mass is obtained on evaporation, from which the acid is expelled by a red heat; at a more moderate heat, the salt is rendered anhydrous: water dissolves it but slowly. It is found native in large quantities in Chili in the form of a white powder ( $\text{Fe}_2\text{O}_3, 3 \text{ SO}_3, 9 \text{ aq.}$ ).

With sulphate of potash and the alkaline sulphates persulphate of iron forms double salts, in form and composition, as well as in taste, resembling common alum. The potash salt ( $\text{KO}, \text{SO}_3, + \text{Fe}_2\text{O}_3, 3 \text{ SO}_3 + 24 \text{ aq.}$  sp. gr. 1.718), is astringent, very soluble in water, but insoluble in alcohol: it is very prone to spontaneous decomposition; and becomes converted from a colourless into a brown, gummy, deliquescent mass: this change is also produced by heating the salt to a temperature below  $212^\circ$ . The solution of the two sulphates should therefore be allowed to evaporate spontaneously during its preparation.

(644) *Protocarbonate of Iron*, ( $\text{FeO}, \text{CO}_2$ , Eq. 58), is found native in immense quantities, forming a valuable ore of iron. In its less usual condition, when crystallized, it constitutes spathic iron ore, and occurs in yellowish lenticular crystals, the primary form of which is a rhombohedron, isomorphous with calcareous spar. The

clay iron ore, from which the greater part of the English iron is obtained, is, as already mentioned, an impure carbonate of iron. Clay iron-stone, besides the more usual form of bands or seams accompanying the coal strata, occurs also in detached nodules or lumps, sometimes of very large size, imbedded in the clay of the same formations. Carbonate of iron is the salt contained in most ferruginous springs, and is held in solution by free carbonic acid: it is rarely present in larger quantity than 1 grain per pint. Mere exposure to air causes its separation; the acid escapes, oxygen is absorbed, and hydrated peroxide of iron, mixed with a small quantity of organic matter, subsides, forming the ochry deposits so usual around chalybeate springs. The protocarbonate of iron may be produced artificially by mixing a protosalt of iron with an alkaline carbonate, when it falls as a pale green voluminous hydrate, which is speedily altered by exposure to air. No percarbonate of this metal appears to exist, but the bicarbonate of potash as well as that of soda dissolves the hydrated peroxide of iron; the red solution thus formed is very slowly decomposed by prolonged ebullition.

(645) PHOSPHATES OF IRON.—*Triprotophosphate of Iron* ( $\text{HO}, 2 \text{FeO}, \text{PO}_5$ ), falls as a white powder on adding triphosphate of soda to a protosalt of iron; by exposure to air it absorbs oxygen, and becomes blue. A hydrated blue phosphate of iron is found native; it is known as *vivianite*. It is probably a mixture of phosphates of the protoxide and peroxide of iron;  $\text{HO}, 2 \text{FeO}, \text{PO}_5 + 2(\text{Fe}_2\text{O}_3, \text{PO}_5)$ , and contains about 30 per cent. of water.

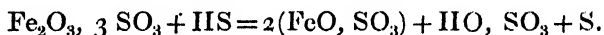
A *sesquiphosphate* ( $\text{Fe}_2\text{O}_3, \text{PO}_5 + 4 \text{aq}$ ), is obtained as a white powder by decomposing sesquichloride of iron by an alkaline triphosphate. Exposure of this salt to air produces no change. It is insoluble in acetic acid, but soluble in peracetate of iron: phosphoric acid is sometimes precipitated in this form in the course of analysis.

(646) CHARACTERS OF THE SALTS OF IRON.—Iron forms two classes of salts, both of which are readily distinguished from each other and from those of other metals. The salts of iron are not poisonous, unless administered in excessive quantities; they form valuable tonics and astringents when taken internally. The solutions both of the protosalts and of the persalts have an inky, astringent taste.

1. *Salts of the Protoxide*.—The protosalts of iron, when in solution, or when crystallized, have a pale green colour; they give no precipitate in acidulated solutions with *hydrosulphuric acid*. With the *alkalies* a grey or green precipitate of hydrated protoxide is

formed; it quickly passes through various shades of green into brown by exposure to the air; this change of colour is due to the absorption of oxygen, in consequence of which the sesquioxide is eventually produced. If the precipitate be produced by *ammonia*, an excess of this reagent redissolves a part of the precipitate; and if the solution contain chloride of ammonium, the whole of the oxide will be redissolved: this solution rapidly absorbs oxygen from the air, and a film of sesquioxide of the metal forms upon the surface. *Red prussiate of potash*, added to a neutral or acid solution gives a bright blue precipitate, which is one of the varieties of Prussian blue. If a solution of a protosalt of iron be boiled with *nitric acid*, the metal is completely converted into a salt of the peroxide: the same thing is effected by the action of chlorine or bromine, or by boiling an acidulated solution of the salt with a small quantity of chlorate of potash.

2. *Salts of the peroxide*.—In solution they have a yellowish or reddish brown colour. *Hydrosulphuric acid* reduces them to the state of protosalts, whilst a white deposit of sulphur occurs: for example, with the persulphate the following reaction takes place:—



With *hydrosulphate of ammonia* a black hydrated sulphide of iron is precipitated. The *alkalies* give a reddish brown voluminous precipitate of hydrated peroxide, insoluble in excess of alkali. *Sulphocyanide of potassium* gives an intense blood-red solution. *Yellow prussiate of potash*, a bright blue precipitate of ordinary Prussian blue. *Tincture of galls* in neutral solutions, a bluish-black, inky precipitate; this test is rendered much more delicate in its indications by the addition of water holding a little bicarbonate of lime in solution: it is the colouring matter of ordinary writing ink. In neutral solutions the *benzoates* and the *succinates* of the alkalies give voluminous insoluble precipitates: benzoate or succinate of ammonia or potash is sometimes employed to separate iron from nickel and cobalt, as the benzoates and the succinates of these metals are soluble. If a solution of a persalt of iron, to which potash has been added till it begins to occasion a permanent precipitate, be raised to the boiling point, it is completely decomposed, and an insoluble subsalt of iron is precipitated: this property is often turned to account in the separation of iron from cobalt, nickel, and manganese, which are not precipitated under similar circumstances.

*Before the blowpipe* both classes of the salts act alike: with borax in the reducing flame they give a green glass, which becomes

colourless, or yellowish (if the iron be in large quantity) when held in the oxidating flame. All the salts of iron give with hydrosulphate of ammonia a black precipitate of sulphide of iron.

(647) *Estimation of Iron.*—In estimating the quantity of iron for the purposes of analysis, it should always be first converted into a persalt, by boiling with nitric acid or otherwise, and precipitated by excess of ammonia, and then well washed and ignited: pure sesquioxide of iron remains, consisting in 100 parts of 70 of iron and 30 of oxygen. Iron is thus readily separated from the alkalies and alkaline earths: If magnesia be present, it is apt to be partially precipitated with the oxide of iron, unless the solution contain a considerable quantity of chloride of ammonium. When tartaric acid, sugar, and various other forms of organic matter are present in the solution, ammonia precipitates the peroxide of iron very imperfectly: in such a case hydrosulphate of ammonia must be employed. The iron is thus thrown down completely as sulphide; this precipitate must be redissolved in nitric acid, and then the iron may be obtained as peroxide by adding an excess of ammonia to the solution.

(648) *Separation of Iron from Alumina and Glucina.*—If alumina and glucina are contained in the liquid, they accompany the peroxide of iron when precipitated by ammonia. When these earths are present, the precipitation should be effected by an excess of caustic potash instead of ammonia; the precipitate should be gently warmed with the liquid for the purpose of dissolving out the earths. The solution is filtered from the oxide of iron, which requires long washing with boiling water to remove the last traces of potash. The alumina and glucina are obtained from the alkaline filtrate by neutralizing it with hydrochloric acid, and then adding a slight excess of ammonia; the alumina and glucina precipitate together, and must be separated in the manner described in (578).

(649) *Separation of Iron from Zinc, Cadmium, Cobalt, Nickel, and Manganese.*—Having precipitated the cadmium by sulphuretted hydrogen, and reconverted the iron into peroxide by boiling the liquid with a small quantity of nitric acid, the solution is digested in the cold upon an excess of pure, finely levigated carbonate of baryta, with frequent agitation: the iron is completely separated in the form of a basic salt of the peroxide, which must be thoroughly washed. This precipitate is then redissolved in hydrochloric acid, and the baryta separated by the addition of dilute sulphuric acid; the iron may afterwards be precipitated by ammonia as usual.

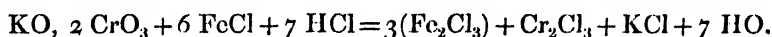
Sometimes ammonia in excess is made use of to separate iron from these metals, which all form soluble compounds with ammo-

nia, and which, it is supposed, will retain them in solution, but this method should never be resorted to in analysis, as the iron always retains a large quantity of the other oxides.

(650) *Separation of Iron from Uranium.*—The iron having been converted into peroxide, is precipitated by a large excess of carbonate of ammonia, which retains most of the uranium. This process, however, although usually adopted, is imperfect: as, if the quantity of iron be at all large, it retains a considerable proportion of uranium.

(651) *Estimation of a mixture of Protoxide and Peroxide of Iron.*—It often happens that the chemist has to ascertain the relative proportions of protoxide and sesquioxide of iron which a compound contains. Many chemists employ for this purpose the process contrived by Margueritte, which consists in ascertaining the quantity of a measured solution of permanganate of potash of known strength, which the solution of iron can deoxidize and deprive of colour (*Ann. de Chimie*, III. xviii. 244).

If the compound of iron for examination be soluble in hydrochloric acid, the following process by Dr. Penny will be found both easy of execution and accurate in its results. It is based upon the power which a solution of bichromate of potash in excess of hydrochloric acid possesses of converting protochloride of iron into perchloride, while the chromium is reduced to the state of sesquichloride, in the manner shown by the following equation:—



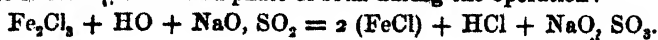
In order to carry this process into effect, 44·4 grains of pure bichromate of potash are introduced into an alkalimeter burette (480), which is to be filled up to 0 with tepid water; the mixture is to be agitated until the salt is dissolved. Each division of the instrument contains sufficient of the bichromate to convert half a grain of <sup>metallic iron present in the form of</sup> protochloride of iron into sesquichloride. The ore for experiment having been reduced to an extremely fine powder, 100 grains of it are boiled in a flask for ten or fifteen minutes with about 2 ounces of hydrochloric acid, of sp. gr. 1·100: about 6 ounces of boiling distilled water are to be added, and the mixture immediately transferred to an evaporating basin, taking care to rinse out the flask thoroughly. A white plate is then spotted over with a few drops of a weak solution of red prussiate of potash, and the bichromate is cautiously added from the alkalimeter to the solution of iron (which is kept in continual agitation), until it assumes a dark greenish shade; as soon as this begins to appear, it must be tested after each addition of the bichromate, by

taking out a drop of the solution on a glass rod, and adding it to one of the drops of the red prussiate. When the last drop no longer occasions a blue precipitate, the operation is ended, and the number of divisions of the liquid which has been added, when multiplied by two, indicates the amount of metallic iron which exists in the form of protoxide in 100 parts of the ore. The total quantity of iron present in the solution may be ascertained by making a second experiment on a fresh portion of the ore, and reducing the metal whilst still in the flask with the hydrochloric acid, to the state of protoxide: this is readily effected by adding a solution of sulphite of soda until a drop of the liquid ceases to give a red colour when mixed with a drop of solution of sulphocyanide of potassium,\* placed upon a white plate: the liquid is then boiled to expel the excess of sulphurous acid. When the iron has thus been reduced to the state of protoxide, the whole quantity of the metal present may be ascertained by means of the solution of bichromate of potash, as before; the difference between the two results will give the per-centage of metallic iron present in the form of peroxide.

(652) *Analysis of Cast-Iron, Steel, and Bar-Iron.*—For this purpose the metal must be reduced to a fine state of subdivision by means of a new file, previously freed from oil by the action of a solution of potash; the fine particles detached are to be sifted through a lawn sieve. Some kinds of cast-iron are too hard to admit of being filed; they must be crushed in a small mortar made of hard steel.

1. The proportion of *carbon* is ascertained by mixing from 50 to 100 grains of finely divided iron with about 10 times its weight of chromate of lead; then placing it in an apparatus similar to that shown in fig. 244, and burning the iron in a very gentle current of oxygen; the carbonic acid which is formed is collected in solution of potash placed in Liebig's bulbs. The tube which contains the iron is gradually heated with charcoal, commencing at the extremity nearest the potash bulbs, and the fire is slowly advanced towards the other end, until, when the operation is completed, the whole length of the tube is red-hot. From the quantity of carbonic acid thus obtained, the proportion of carbon in the iron may be calculated. But it has been already explained that cast-iron contains carbon partly in chemical combination, partly

\* The reducing effect of sulphite of soda on the perchloride of iron may be explained by the following equation, from which it will be seen that the sulphite is converted into sulphate of soda during the operation:—



in a state of mechanical mixture, and it is important to determine the relative proportions of the carbon which exist in these different conditions. This may be effected by dissolving the iron in hydrochloric acid. In this operation all the carbon which was chemically combined with the iron is separated in the form either of a gaseous compound of carbon and hydrogen, or as a liquid hydrocarbon; whilst the scales of graphite mechanically diffused through the metal are not acted upon by the acid, and are left in a solid form mixed with silica. In order to ascertain the proportion of graphite in this residue, it is collected on a small weighed filter, and washed with ether to remove any adhering liquid hydrocarbon; the filter and its contents are dried at  $212^{\circ}$  F., and weighed in a covered crucible. The residue is then burned, and the silica which remains is deducted from the weight of the precipitate collected on the filter.

2. The quantity of *silicon* contained in the iron is ascertained by dissolving the metal in hydrochloric acid and evaporating the solution to dryness, moistening with concentrated hydrochloric acid, thus dissolving all the soluble matter in water, and collecting the silica on a filter: from this residue, after the graphite is burned off, the quantity of silicon can be estimated, 100 parts of silicic acid representing 48 of silicon.

3. *Sulphur, Phosphorus, and Arsenic.*—The most accurate mode of estimating these substances consists in deflagrating about 50 grains of the finely-divided iron with about six times its weight of a mixture of 5 parts of pure nitre, and 1 part of carbonate of potash, in a crucible of silver, or, still better, of gold.\* The phosphorus, sulphur, and arsenic are thus converted into phosphoric, sulphuric, and arsenic acids, and combine with the potash; when the fused mass is digested in water they are dissolved, whilst the oxide of iron remains undissolved. The filtered solution is supersaturated with hydrochloric acid, and the sulphuric acid is thrown down by means of chloride of barium; the excess of baryta is removed by adding sulphuric acid, and the arsenic is thrown down by a current of sulphuretted hydrogen. The liquid, filtered from sulphide of arsenic, is now neutralized by ammonia, and on the addition of a few drops of solution of sulphate of magnesia, the phosphoric acid is gradually separated, on standing, as the crystalline double phosphate of magnesia and ammonia.

\* Any traces of vanadium or of chromium would also be oxidized, and on digesting the mass in water would dissolve out in the alkaline liquid.



The oxide of iron is dissolved in hydrochloric acid, and a current of sulphuretted hydrogen is transmitted, by which copper would be separated as sulphide; the filtrate is boiled with nitric acid, and the iron separated from manganese, cobalt, or nickel by means of carbonate of baryta in the manner already described (649).

## § VII. CHROMIUM.

*Symbol, Cr; Equivalent, 26.27; Specific Gravity, 5.9.*

(653) CHROMIUM is a metal which is but sparingly distributed over the earth. Its most important ore is the chrome iron-stone, a compound of protoxide of iron and sesquioxide of chromium ( $\text{FeO}$ ,  $\text{Cr}_2\text{O}_3$ ), which has now and then been met with crystallized in regular octohedra like the magnetic oxide of iron, to which it corresponds in composition; but is more generally found massive: it is principally supplied from the United States and from Sweden. Occasionally the metal occurs in a higher state of oxidation, in combination with oxide of lead, as chromate of lead ( $\text{PbO}$ ,  $\text{CrO}_3$ ). Indeed it was in this beautiful mineral that Vauquelin in the year 1797 first discovered the existence of chromium.

To obtain the pure metal, oxide of chromium is intimately mixed, in fine powder, with charcoal, and made up into a paste with oil; it is then placed in a crucible lined with charcoal, and the cover of the crucible is luted on, after which it is exposed for two hours to the heat of a good wind furnace; an agglomerated mass, of metallic appearance, is thus obtained. It is not pure chromium, but consists of a combination of carbon with the metal. Chromium obtained by this method is very difficult of fusion; it generally forms a porous mass composed of brilliant grains, which are hard enough to scratch glass. In this state it has a specific gravity of about 5.9. If ignited with the alkalies, alkaline carbonates, or nitrates, it is rapidly converted into chromic acid, which combines with the alkaline base. It may, however, be heated to redness in the open air, without becoming oxidized, and is not acted on by any acid except the hydrochloric acid.

Another modification of the metal may be procured by decomposing its sesquichloride by heating it with potassium; after washing the residue with water, the metal remains in the form of a dark grey powder, which assumes a metallic lustre under the burnisher. This pulverulent chromium, if heated in the air, takes fire below redness, and burns brilliantly. It is oxidized with great violence by

nitric acid, sometimes becoming incandescent during the action; it is dissolved by hydrochloric acid and dilute sulphuric acid, with evolution of hydrogen.

Metallic chromium has not been applied in the arts, but its oxide and many of the chromates are highly valued as colouring materials, both in painting on porcelain and in calico printing.

(654) *Compounds of Chromium with Oxygen.*—Chromium forms 4 well marked oxides; a protoxide,  $\text{CrO}$ ; a sesquioxide,  $\text{Cr}_2\text{O}_3$ , both capable of forming salts with acids: an intermediate oxide ( $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3$ ), corresponding to the magnetic oxide of iron, and a powerful metallic acid ( $\text{CrO}_3$ ), chromic acid, corresponding to manganic and ferric acids. It also appears probable that a perchromic acid ( $\text{Cr}_2\text{O}_7$ ) exists; at least a blue liquid is obtained on pouring peroxide of hydrogen into a solution of chromic acid.

*Protoxide of Chromium* ( $\text{CrO}$ ); *Eq.* 34·3—This oxide is known only in the hydrated condition. It is obtained as a dark brown precipitate on adding caustic potash to a solution of the protochloride of chromium; it absorbs oxygen with great avidity, and even decomposes water, with extrication of hydrogen, and then becomes converted into the intermediate hydrated oxide ( $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{H}_2\text{O}$ ), which is of the colour of Spanish snuff.

The protoxide of chromium forms a double sulphate with sulphate of potash ( $\text{CrO}$ ,  $\text{SO}_3 + \text{KO}$ ,  $\text{SO}_3$ , 6 aq), corresponding to the double sulphate of iron and potash both in form and composition. The crystals are of a fine blue colour.

(655) *Sesquioxide* ( $\text{Cr}_2\text{O}_3$ ); *Eq.* 76·5; *Sp. Gr. crystallized*, 5·21.—This oxide is obtained as a greyish-green hydrate by boiling with alcohol a solution of bichromate of potash acidulated with sulphuric acid. The alcohol deprives the chromic acid of half its oxygen, and the liquid becomes green from the formation of a sulphate of the sesquioxide. On the addition of ammonia, a bulky, gelatinous, green precipitate of the hydrated oxide is produced, which, when dried in the air, has the formula ( $\text{Cr}_2\text{O}_3$ , 10 aq). In this form it is freely soluble in acids, and forms salts the solutions of which are of a green colour; but they do not crystallize. Sesquioxide of chromium, though comparatively a feeble base, forms also another isomeric set of soluble salts, which are of a violet colour. If these violet-coloured salts be precipitated by an alkali, they give a bluish-green hydrated oxide, which if redissolved in an acid without the application of heat, reproduces the violet-coloured salts. If the liquid be heated to the boiling point, or a little short of it, the salt passes at once into the green modification. The violet salts

crystallize readily. The oxide, from the violet salts is soluble in excess of ammonia; and by long digestion with strong ammonia the green modification of the oxide passes into the violet, and is dissolved by the alkali. Potash and soda precipitate the hydrated oxide from both varieties, and redissolve it if added in excess, forming a green solution, from which, on boiling, the whole of the oxide of chrome separates as the hydrate of the green salts. The hydrate thus obtained, according to Fremy, contains 9 equivalents of water; ( $\text{Cr}_2\text{O}_3, 9 \text{HO}$ ). When the hydrated oxide is heated, it parts with its water below redness, after which it is much less soluble in acids. If heated a little beyond this point, it suddenly becomes incandescent, shrinks considerably in bulk, and is no longer attacked by acids. Besides the two soluble varieties of the salts of chrome before mentioned, a third anhydrous, insoluble series is known, corresponding, it would seem, to the dense and comparatively inert modification of the metal itself.

The green oxide of chrome is not decomposed by heat, and hence is used as a green colour in enamel painting. It is usually prepared for this purpose by decomposing chromate of mercury by a red heat: half the oxygen of the acid is expelled along with the oxide of mercury. Chromate of ammonia may be employed instead of chromate of mercury with equally good results. Another method consists in strongly igniting, in a covered crucible, an intimate mixture of 4 parts of powdered bichromate of potash and 1 part of starch; the carbonate of potash resulting from the decomposition is washed out, and the oxide of chrome which remains, after undergoing a second calcination, yields a beautiful clear green colour. There are also a variety of other modes of obtaining it. Oxide of chrome is the colouring ingredient in greenstone, in the emerald, in pyrope, and in several other minerals. The pink colour used on earthenware is prepared by heating to redness a mixture of 30 parts of peroxide of tin, 10 of chalk, and 1 of chromate of potash; the product is then finely powdered, and washed with weak muriatic acid; a beautiful rose-tint is thus obtained.

(656) *Chromic Acid* ( $\text{CrO}_3$ ); *Eq.* 50·3, *Sp. Gr.* 2·676.—There are several modes of obtaining this compound. The simplest consists in mixing 4 measures of a cold saturated solution of bichromate of potash with 5 of oil of vitriol: as the liquid cools, the chromic acid separates in beautiful crimson needles; for though very soluble in water, the acid has the peculiarity of being nearly insoluble in sulphuric acid of *Sp. Gr.* 1·55, but is freely dissolved by it either in a more concentrated, or in a more dilute condition.

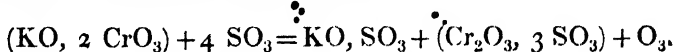
## CHROMIC ACID—CHROMATES OF POTASH.

The crystals are allowed to dry upon a porous tile, under a bell-glass. A good deal of sulphuric acid however still adheres to them: M. Fritsche recommends, in order to remove this sulphuric acid, that the crystals should be dissolved in water, and a solution of bichromate of baryta should be added in quantity just sufficient to throw down the whole of the sulphuric acid as sulphate of baryta: the solution may be recrystallized by evaporation in vacuo.

Chromic acid when dried at a gentle heat is anhydrous. While hot it is black, but becomes dark red on cooling: at about 400° F. it fuses, and if heated more strongly, becomes vividly incandescent, and is converted into the sesquioxide with disengagement of oxygen. Chromic acid deliquesces when exposed to the air. It has a sour, metallic taste, and possesses considerable oxidizing power, from the facility with which it is reduced to sesquioxide of chromium. Chromic acid forms more than one crystalline compound with sulphuric acid: these compounds are decomposed by water.

*Chromates.*—Chromic acid combines with bases, and forms three classes of salts—basic, neutral, and acid. The chromates of the alkalis are soluble in water; the neutral salts have a yellow colour; the acid salts are of a bright orange: the most important of these salts are the chromate and bichromate of potash, from which the other chromates are generally obtained.

The *bichromate of potash* ( $\text{K}_2\text{O}, 2 \text{CrO}_3$ , *Eq.* 147·5, *Sp. Gr.* 2·624), crystallizes in large red, transparent, anhydrous 4-sided tables. It fuses below redness, and as it cools splits to pieces from the inequality of its contraction. It requires about 10 times its weight of water at 60° for its solution. When heated with sulphuric acid, oxygen gas is evolved, and sulphate of potash and sulphate of sesquioxide of chromium are formed:—



If a solution of carbonate of potash be added to the bichromate, until it becomes of a pale yellow colour, carbonic acid is expelled, and the *neutral chromate* ( $\text{K}_2\text{O}, \text{CrO}_3$ , *Eq.* 97·3, *Sp. Gr.* 2·682), is formed. This salt dissolves in about twice its weight of cold water, and still more freely in boiling water; it has a pure and intense yellow colour. A very small quantity of the salt suffices to impart a yellow tinge to a considerable volume of water. By evaporation chromate of potash may be obtained with some difficulty, in transparent, yellow, anhydrous prisms, which are isomorphous with those of sulphate of potash; at a red heat it fuses without under-

going decomposition. A *terchromate of potash* ( $\text{KO}, 3 \text{CrO}_3$ ), also anhydrous, was obtained by Mitscherlich in deep red crystals, by adding an excess of nitric acid to a solution of the bichromate, and allowing it to evaporate.

To procure the bichromate of potash, chrome ironstone is reduced to an extremely fine powder, and heated in a reverberatory furnace with carbonate of potash and a small proportion of nitre, the mixture being constantly stirred, to hasten the oxidation. When this is complete, the product is digested in water, and the yellow solution is drawn off from the insoluble matter; it is then supersaturated with nitric acid; a portion of silica is precipitated, and after this has been separated, the liquid, on evaporation, yields crystals of bichromate of potash, which are purified by recrystallization.

According to M. Schweitzer several double salts may be formed by digesting bichromate of potash with an equivalent of some other base, such as lime or magnesia. The chromate of magnesia and potash crystallizes in oblique rhombic prisms, ( $\text{KO}, \text{MgO}, 2 \text{CrO}_3 + 2 \text{H}_2\text{O}$ ) and a salt of similar composition may be obtained with lime.

*Chromate of Soda* ( $\text{NaO}, \text{CrO}_3$ , 10 aq, *Eq.* 81.3 + 90), may be obtained in a similar manner to the chromate of potash; it crystallizes like the sulphate of soda with 10 equivalents of water: a bichromate of soda may likewise be formed.

*Bichromate of Lime* is formed in many chrome works as a preliminary stage in the manufacture of the chromates. Jacquelin decomposes chrome ore by roasting it in fine powder intimately mixed with chalk, grinds the roasted mass with water, and adds sulphuric acid till the liquid has an acid reaction, in which case bichromate of lime is formed, and remains in solution.

*Chromate of baryta* is a canary yellow insoluble powder. *Chromate of strontia* is yellow and soluble. *Subchromate of mercury* ( $4 \text{Hg}_2\text{O}, 3 \text{CrO}_3$ ), falls as an orange-coloured insoluble precipitate on adding subnitrate of mercury to a soluble chromate. *Chromate of silver* ( $\text{AgO}, \text{CrO}_3$ , *Sp. Gr.* 5.770), is of a dark red colour, the tint of which is deeper if the solutions be mixed whilst hot: it is crystalline, and sparingly soluble.

*Chromate of Lead* ( $\text{PbO}, \text{CrO}_3$ , *Eq.* 162.3, *Sp. Gr.* 5.653), forms the pigment called 'chrome yellow.' It is obtained by precipitating solution of acetate of lead by one of chromate or of bichromate of potash. Chromate of lead is insoluble in water, or in acids, but like all the insoluble salts of lead, it is dissolved by a large excess of potash or soda. A *Dichromate of Lead* ( $2 \text{PbO}, \text{CrO}_3$ , *Sp. Gr.* 6.266), of a splendid scarlet colour, may be obtained by adding to a solution of nitrate of lead a solution of chromate of

potash, with which an additional equivalent of hydrate of potash has been previously mixed. It may be obtained of a still more brilliant colour by fusing 1 part of the neutral chromate of lead with 5 parts of nitre; chromate of potash and dichromate of lead are formed; the salt of potash may be removed by washing.

• Chromic acid is the colouring matter of the ruby.

*Bichromate of Chloride of Potassium* ( $\text{KCl}$ , 2  $\text{CrO}_3$ ).—This remarkable compound may be obtained crystallized in orange-coloured needles, by dissolving 3 parts of bichromate of potash, and 4 of hydrochloric acid, in a little water at a gentle heat, and allowing it to cool; a large quantity of water decomposes the salt.

(656 bis) *Sesquisulphide of Chromium* ( $\text{Cr}_2\text{S}_3$ ), *Eq.* 100.5.—This compound may be obtained in black shining scales, resembling plumbago in appearance, when the vapour of bisulphide of carbon is transmitted over sesquioxide of chromium strongly heated in a porcelain tube. The affinity of chromium for sulphur is but slight. If the hydrosulphate of ammonia be mixed with a salt of the sesquioxide of chrome, the hydrated sesquioxide of the metal is precipitated, whilst sulphuretted hydrogen is evolved.

(657) *Chlorochromic Acid*,  $\text{CrClO}_2$ , or ( $\text{CrCl}_3 + 2 \text{CrO}_3$ ) is a dense red liquid, which emits copious red fumes of suffocating odour; it is immediately decomposed by water into chromic and hydrochloric acids. When dropped into strong solution of ammonia it bursts into flame from the intensity of the reaction. If the vapour be passed through a tube of porcelain heated to redness, beautiful rhombohedral crystals of sesquioxide of chromium are formed; these crystals are isomorphous with those of corundum; they are hard enough to cut glass, and are of a very dark green colour. During their formation, oxygen and chlorine escape in consequence of the following reaction;  $2 (\text{CrClO}_2) = \text{Cr}_2\text{O}_3 + \text{Cl}_2 + \text{O}$ .

Chlorochromic acid is analogous to the chloromolybdic, chlorotungstic, and chlorosulphuric acids in composition, and in the products which it yields when decomposed. In order to prepare it, 10 parts of common salt are fused with 17 of chromate of potash; the melted mass, when cold, is broken into fragments, and gently heated in a retort, with 30 parts of oil of vitriol. The chlorochromic acid distils over readily.

(657 bis) *Compounds of Chromium with Chlorine*.—Besides the preceding, chromium forms two compounds with chlorine,—a protochloride and a sesquichloride. The latter is the more important.

*Sesquichloride of Chromium* ( $\text{Cr}_2\text{Cl}_3$ ), *Eq.* 159.—When a current of dry chlorine is transmitted over an intimate mixture of finely

divided sesquioxide of chromium and charcoal, heated to redness in a glass tube, beautiful scales of the anhydrous sesquichloride of the metal sublime, of a pale violet colour; when rubbed upon the skin they have a soapy feel; they are quite insoluble in cold water, but by boiling them with water for some time a green solution is gradually formed. Sulphuric and hydrochloric acids, and even aqua regia do not dissolve them. It is however very remarkable that the change from this insoluble to the soluble green variety, is effected in a few moments with extrication of heat, by the addition of a minute quantity of the protochloride of chromium. When the green hydrated sesquioxide of chrome is dissolved in hydrochloric acid, a similar green solution is formed: the liquid furnishes, by spontaneous evaporation, green crystals, which may be represented, according to Peligot, as consisting of  $(\text{Cr}_2\text{O}_2\text{Cl} + 2 \text{HCl} + 10 \text{HO})$ ; but it is singular that only two-thirds of the chlorine which this solution contains is precipitated when it is mixed with nitrate of silver, (*Ann. de Chimie*, III., xii., 536; xiv., 239, and xiv., 294.) A violet chloride of the metal which contains the same proportion of chlorine may be formed by precipitating the violet-coloured sulphate of chrome by an equivalent quantity of chloride of barium: nitrate of silver precipitates the whole of the chlorine from this solution.

Several oxychlorides of chrome may be formed.

*Protochloride of Chromium* ( $\text{CrCl}$ ), *Eq.* 61·7, is obtained by heating the sesquichloride to redness in a current of dry hydrogen (carefully freed from every trace of oxygen); it is a white substance which is readily dissolved by water, forming a blue solution which rapidly absorbs oxygen.

(658) The *Terfluoride of Chromium* ( $\text{CrF}_3$ ) *Eq.* 83·3, is obtained by distilling 4 parts of chromate of lead, 3 of powdered fluor spar, and 8 of strong sulphuric acid, in a platinum retort; sulphates of lead and of lime are formed, and the terfluoride distils as a deep red vapour, which by a low temperature is reduced to a blood-red liquid. The reaction which attends its formation may be thus represented;  $\text{PbO}, \text{CrO}_3 + 3 \text{CaF} + 4 (\text{HO}, \text{SO}_3) = \text{PbO}, \text{SO}_3 + 3 (\text{CaO}, \text{SO}_3) + 4 \text{HO} + \text{CrF}_3$ .

Terfluoride of chromium forms deep red fumes of chromic acid the moment that it comes into the air, as it is instantly decomposed by moisture: by conducting the vapour into a moistened platinum crucible the vessel speedily becomes filled with voluminous crystals of chromic acid, from which the hydrofluoric acid may be expelled by a gentle heat. The formation of the chromic acid is readily accounted for as follows;  $\text{CrF}_3 + 3 \text{HO} = \text{CrO}_3 + 3 \text{HF}$ .

(659) *Nitride of Chromium*  $\text{Cr}_3\text{N}_2$ ? (Schrötter).—If the anhydrous sesquichloride of chromium be heated in a current of dry ammoniacal gas, chloride of ammonium sublimes, whilst the chloride of chromium is decomposed, emitting a purple light, and an insoluble chocolate brown compound of chromium and nitrogen is left. If it be heated to between  $300^\circ$  and  $400^\circ$  F., in a current of oxygen, it takes fire, and burns with a beautiful red light into oxide of chromium, emitting nitrogen gas mixed with red fumes of peroxide of nitrogen.

(659 bis) *Sulphate of Chromium*,  $(\text{Cr}_2\text{O}_3, 3 \text{ SO}_3)$ ; Eq. 196.5.—There are three varieties of this salt. One of them is a *green* soluble compound, which is freely dissolved by alcohol, but does not crystallize. It may be obtained by boiling either of the hydrated oxides of chromium with sulphuric acid. A second modification, of a *violet* colour, may be procured by digesting 8 parts of the hydrated oxide of chromium dried at  $212^\circ$  with 9 parts of oil of vitriol, in a shallow vessel exposed to the air at ordinary temperatures. The mixture gradually absorbs water, and becomes converted in two or three weeks' time into a greenish-blue mass of crystals: these crystals are dissolved by water, and form a blue liquid, from which alcohol separates the salt in crystalline grains. This modification forms with sulphate of potash, or with sulphate of ammonia, a beautiful violet double salt (chrome alum) which crystallizes by spontaneous evaporation in bold octohedra, and corresponds in form and composition to ordinary alum, the formula of the potash salt being  $(\text{KO}, \text{SO}_3 + \text{Cr}_2\text{O}_3, 3 \text{ SO}_3, + 24 \text{ aq.})$ , *sp. gr.* 1.826. The solution of the violet sulphate, when boiled, becomes green; and if the crystals of chrome alum be dissolved in water, and the solution be boiled, the plum-coloured liquid also becomes green, and loses the power of crystallizing on cooling. If the violet sulphate be heated to  $212^\circ$  it melts in its water of crystallization, loses 10 equivalents of water, and becomes converted into the green salt: but if the temperature be raised to about  $700^\circ$ , both the green and the violet modification are rendered anhydrous, and a third salt is obtained in *red* crystals, which are no longer soluble in water, or even in concentrated acids, or aqua regia. If digested for a long time with water, however, it becomes converted into the soluble form (Schrötter, Poggendorff, *Annal.* liii., 513). The composition of these three sulphates would be represented as follows:—

Red insoluble sulphate . . .	$\text{Cr}_2\text{O}_3, 3 \text{ SO}_3$
Green soluble sulphate . . .	$\text{Cr}_2\text{O}_3, 3 \text{ SO}_3, 5 \text{ H}_2\text{O}$
Violet soluble sulphate . . .	$\text{Cr}_2\text{O}_3, 3 \text{ SO}_3, 15 \text{ H}_2\text{O}$



Several subsulphates of chrome may also be formed.

*The Nitrate of Chromium* is a green very soluble salt; when gently ignited, it loses its acid, and yields a brown oxide of chrome ( $\text{CrO}_2$ ) which is regarded as a chromate of sesquioxide of chrome ( $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$ ).

(660) CHARACTERS OF THE COMPOUNDS OF CHROMIUM :—

1. The *Salts of the Protoxide* are but little known. They rapidly absorb oxygen from the air; they are sparingly soluble in water, and form either red or blue solutions. *Potash* gives a brown precipitate of hydrated protoxide of chromium in these solutions; *ammonia*, a greenish white precipitate, which if hydrochlorate of ammonia be present is redissolved by excess of ammonia, forming a blue liquid which becomes red as it absorbs oxygen. With *sulphide of potassium* they give a black sulphide; and with *ferrocyanide of potassium* a greenish yellow precipitate. These salts reduce solutions of gold to the metallic state, and convert corrosive sublimate into calomel.

2. The *Salts of the Sesquioxide* have a sweetish astringent taste. They are either green or violet coloured; the green solutions generally transmit a red light. With *ammonia* they yield a bulky gelatinous precipitate of hydrated sesquioxide of chrome. *Potash and Soda* give a green precipitate, which is dissolved with a green colour, in excess of the cold alkaline solution, but is re-precipitated completely by boiling the liquid. The *alkaline carbonates* give a green precipitate which is redissolved by an excess of the alkaline liquid. *Sulphuretted hydrogen* gives no precipitate. The *alkaline sulphides* precipitate the green sesquioxide of chromium, with escape of sulphuretted hydrogen. If any of these precipitates be fused with nitre, it yields a yellow soluble chromate of potash.

3. The *Chromates*.—Before the blowpipe they colour borax and microcosmic salt green. When boiled with dilute sulphuric acid, to which a little alcohol or sugar has been added, they are decomposed, and the chromic acid is reduced to the green oxide of chrome, which is dissolved by the sulphuric acid, and is precipitated with its characteristic colour on neutralizing with ammonia. Most of the chromates are strongly coloured. Their solutions give a yellow precipitate with *salts of lead*, a red with *nitrate of silver*, and an orange with *subnitrate of mercury*.

(661) *Estimation of Chromium, and separation from the Alkalies and Alkaline Earths*.—Chromium may be most accurately estimated in the form of sesquioxide. It may be easily reduced

to this condition even if it exist in solution in the form of a chromate, by acidulating with hydrochloric acid, and transmitting a current of sulphuretted hydrogen: the liquid must then be boiled, and on the addition of ammonia to the hot solution the oxide of chromium is precipitated. It is to be well washed and ignited in a covered platinum crucible; 100 parts of the anhydrous oxide contain 68.68 of chromium.

The *Separation of Chromium from the Earths, and from Zinc, Cadmium, Cobalt, Nickel, and Iron* may be effected by fusing the mineral, or the precipitate obtained by ammonia from its solution in an acid, with a mixture of carbonate of potash and nitre, the chromium is thus converted into chromic acid, and forms a soluble compound, from which the chromium may be precipitated as directed in the foregoing paragraph, whilst the earths and the other metals remain in the insoluble portion, either in the form of oxides or of carbonates.

#### § VIII. MANGANESE.

*Symbol*, Mn; *Equivalent*, 27.57; *Specific Gravity*, 8.013.

(662) The ores of this metal are tolerably abundant, and it enters into the composition in greater or less quantity of a vast number of minerals, so that it is widely diffused throughout the mineral kingdom. The most important and valuable ore of manganese is the black oxide, which occurs either massive or in radiated crystals.

Manganese is reduced to the metallic state with difficulty. The best method consists in mixing the carbonate into a paste with oil and sugar, and igniting it intensely for a couple of hours in a crucible lined with charcoal, furnished with a cover luted on, and exposed to the heat of a forge. It may thus be obtained in a metallic globule which contains a variable quantity of carbon; the carbon may be removed by fusing the metal a second time in a porcelain crucible with a little carbonate of manganese.

Manganese is of a greyish white colour, and is brittle, but hard enough to scratch steel; it is very feebly magnetic. By exposure to the air, it speedily becomes oxidated, and should be preserved either in sealed tubes or under naphtha.

Manganese enters into combination both with carbon and silicon when fused with them: the carbide, when treated with acids, leaves part of the carbon as a black powder: the compound of manganese with silicon is decomposed with difficulty even by aqua

regia, in which case it leaves a residue of silicic acid. The chief uses of the compounds of manganese are chemical, the peroxide being extensively employed to decompose muriatic acid and furnish chlorine. It likewise supplies the chemist with his cheapest source of oxygen, and is employed as a colouring material in the manufacture of glass and enamels. It combines with iron, and increases its hardness and elasticity, and is hence useful in the manufacture of steel.

(663) *Compounds of Manganese with Oxygen.*—Manganese forms several compounds with oxygen. The protoxide,  $\text{MnO}$ , is a powerful base; the sesquioxide,  $\text{Mn}_2\text{O}_3$ , is feebly basic; the red oxide, a compound of these two,  $\text{MnO}, \text{Mn}_2\text{O}_3$ , is quite indifferent to the action of acids; so also is the deutoxide or black oxide,  $\text{MnO}_2$ ; but the two higher oxides have well marked acid characters. The formula for manganic acid is  $\text{MnO}_3$ , and that for permanganic acid  $\text{Mn}_2\text{O}_7$ . Neither of these acids, however, can be obtained except in combination with water or a metallic oxide.

The *protoxide*, ( $\text{MnO}$ , *Eq.* 35.5), may be obtained easily by igniting carbonate of manganese in a current of hydrogen; it is of an olive-green colour, and unless it has been strongly heated, absorbs oxygen from the air; if ignited in the air it burns, and is converted into a brown superior oxide. It may be obtained as a white hydrate by decomposing a salt of manganese by any alkali, but it immediately begins to absorb oxygen from the air, and turns brown. It is soluble in ammonia, especially if the solution contain an ammoniacal salt. The protoxide unites with acids, forming well-characterized salts.

*Sesquioxide*, ( $\text{Mn}_2\text{O}_3$ ), *Eq.* 79, *Sp. Gr.* 4.82.—This oxide is found in its anhydrous form in acute octohedra, constituting *brownite*; it occurs naturally in a hydrated state in *manganite*, which is of a blackish brown colour, and forms brilliant prismatic crystals, ( $\text{Mn}_2\text{O}_3, \text{aq}$ ). The sesquioxide of manganese may be obtained as a brown hydrate, by passing chlorine through the carbonate of the protoxide suspended in water, and afterwards removing the excess of the carbonate by dilute nitric acid. Sulphuric acid dissolves it slowly, and forms a deep red solution with it, and hydrochloric acid in the cold also forms a soluble compound with it; if these solutions be heated they are decomposed, and a salt of the protoxide is formed. When ignited, the sesquioxide loses one-eighth of its oxygen, and leaves the red oxide.

*Binoxide or peroxide*, ( $\text{MnO}_2$ ), *Eq.* 43.5, *Sp. Gr.* 4.94.—This oxide is the black manganese of commerce and the *pyrolusite* of mineralogists. It is found in steel-grey rhombic prisms. *Psilomelane*

is a black stalactitic or amorphous variety frequently mixed with one of the lower oxides of the metal. *Wad* is also a hydrated peroxide of manganese, with a variable amount of water; it is in a less compact form than psilomelane, and is of a brown colour. Small quantities of cobalt and of the carbonates of the earths are frequent constituents of these ores. Binoxide of manganese is a good conductor of electricity, and is strongly electro-negative in the voltaic circuit. When ignited it gives off one-third of its oxygen, and the red oxide is left;  $3 \text{MnO}_2 = (\text{MnO} \cdot \text{Mn}_2\text{O}_3) + \text{O}_2$ : if heated with concentrated sulphuric acid, half its oxygen escapes, and a protosulphate is formed;  $\text{MnO}_2 + \text{HO}, \text{SO}_3 = \text{MnO}, \text{SO}_3 + \text{HO} + \text{O}$ . With hydrochloric acid chlorine is abundantly evolved, and a protochloride of manganese is left. Nitric acid has but little effect upon it. Peroxide of manganese is procured in a hydrated form as a reddish brown powder, when manganate or permanganate of potash is decomposed by an acid. When the red oxide is treated with nitric acid, a hydrate of the peroxide is left, containing  $4 \text{MnO}_2 + \text{aq}$ .

(664) *Commercial Assay of Oxide of Manganese*.—The commercial value of black oxide of manganese depends upon the proportion of chlorine which a given weight will liberate when it is heated with hydrochloric acid. This quantity of chlorine varies much in different samples, and is dependent upon the proportion of oxygen which the oxide of manganese contains in excess of that which is necessary to its existence as protoxide. A convenient method of estimating this excess of oxygen is founded upon the circumstance that the black oxide of manganese is decomposed in the presence of oxalic acid and free sulphuric acid; protosulphate of manganese is formed, and all the excess of oxygen reacts upon the oxalic acid and converts it into carbonic acid, which passes off with effervescence. If the mixture be weighed before the decomposition is effected, and again after it has been completed, the loss will indicate the amount of carbonic acid; and from this the available amount of oxygen is readily calculated. The reaction may be traced thus:  $\text{MnO}_2 + \text{SO}_3 + \text{C}_2\text{O}_3$  yields  $\text{MnO}, \text{SO}_3 + 2 \text{CO}_2$ . Each equivalent of peroxide of manganese gives 2 equivalents, or exactly its own weight of carbonic acid.

The apparatus of Will and Fresenius, fig. 291, p. 740, is well adapted to the performance of this experiment: 100 grains of the manganese to be tested is reduced to an extremely fine powder, and mixed with 150 grains of oxalic acid; the mixture is placed in the flask, *a*, and about  $1\frac{1}{2}$  ounce of water is added: the experiment is then proceeded with exactly as in the method already described for estimating carbonic acid in a carbonate (481). The decomposition

of the ore is known to be complete as soon as all the black particles have disappeared.

If the sample of manganese contain a carbonate of any of the earths, as may readily be ascertained by the effervescence which will be occasioned on moistening a portion of the oxide with dilute nitric acid, it will be necessary to remove this carbonate. This is easily done by washing the weighed portion with nitric acid diluted with from 16 to 20 parts of water in the flask itself; as soon as the effervescence has ceased, the acid liquid must be carefully poured off, and the flask filled up once or twice with distilled water; the oxide must be allowed to subside; in order to retain any suspended particles, the washings may be thrown upon a small filter, which is afterwards introduced into the flask, and the experiment is then proceeded with as usual.

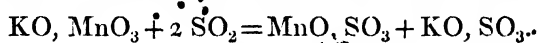
The *Red Oxide*, ( $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ , *Eq.* 114.5), corresponds to the black oxide of iron; it is formed by igniting any of the oxides of manganese in the open air: it occurs native in *hausmannite*, either massive or in four-sided pyramidal crystals of a black colour. The oxide is soluble in phosphoric and in sulphuric acid.

(665) *Manganic Acid*, ( $\text{MnO}_3$ ), *Eq.* 51.5.—When equal weights of caustic potash and peroxide of manganese are fused together, a substance is formed which, when dissolved in a small quantity of water, has a green colour, but which, when largely diluted, becomes purple, and ultimately claret-coloured. This substance has been long known, owing to these changes of colour, under the name of *mineral chameleon*. The colouring material is manganic acid, which, when in combination with potash, has a green colour; it is an unstable compound, and readily either parts with oxygen, or absorbs a larger amount of it, in the latter case forming a red compound; and hence these changes of colour are produced.

Manganic acid has never been obtained except in combination with some powerful base. It may be procured by heating finely powdered peroxide of manganese with its own weight of hydrate of potash, of soda, or baryta; if the green mass thus obtained be heated with a small quantity of cold water, it is partially dissolved, forming a green solution, from which the manganate of the base may be obtained in crystals by evaporating it in vacuo over sulphuric acid. These crystals are isomorphous with the corresponding sulphates and chromates. Manganate of potash, ( $\text{KO}$ ,  $\text{MnO}_3$ ), is anhydrous, and readily soluble in water. It has a very intense colouring power; this fact enables manganese in very minute quantity to be detected before the blowpipe; the material supposed to contain it is fused upon platinum foil, with a little carbonate of potash or

of soda; if any trace of manganese be present, a green colour is imparted to the fused mass. The manganates are very unstable; they are decomposed by boiling their solutions.

In the solid form they are readily decomposed by elevation of temperature, and oxygen is evolved; an excess of potash renders the salt more stable: organic matter also readily abstracts oxygen from them. Their solutions must not even be filtered through paper. Sulphurous and phosphorous acids readily reduce the manganates to a salt of protoxide of manganese; sulphurous acid and manganate of potash, for example, produce the following result:—



(666) *Permanganic Acid*, ( $\text{Mn}_2\text{O}_7$ ), *Eq.* 111.—If a solution of manganate of potash be largely diluted with water, the colour changes from green to violet; the manganic acid passes to a higher state of oxidation, and permanganate of potash is formed.

This salt is best prepared by mixing intimately 4 parts of finely powdered peroxide of manganese with  $3\frac{1}{2}$  parts of chlorate of potash; 5 parts of hydrate of potash are dissolved in a small quantity of water, and added to the mixture, which is dried and reduced to powder, and then heated to dull redness for an hour in an earthen crucible. When cold, the mass is treated with a large quantity of water; the solution on evaporation yields beautiful red acicular crystals of permanganate of potash, ( $\text{KO}, \text{Mn}_2\text{O}_7$ ). These crystals are isomorphous with those of perchlorate of potash; they require about 16 parts of cold water for solution. Permanganate of potash is in certain cases a useful oxidizing agent: it may be employed to detect the occurrence of sulphurous acid in solution in sulphuric or hydrochloric acid; sulphurous acid quickly deoxidizes it and destroys its colour if present.

The permanganates are much more stable than the manganates; their solutions may be boiled without undergoing decomposition. Organic matter, however, combines with part of the oxygen contained in the acid, and reduces it first to manganic acid and then to the binoxide of the metal, which is precipitated as a hydrate in flocculi: their solutions, therefore, must not be filtered through paper, but through a funnel loosely plugged with asbestos. When ignited, oxygen is given out, and a manganate is reproduced, which, if the heat be too great, is in turn decomposed with a further extrication of oxygen. Most of the permanganates are freely soluble in water; the permanganate of silver is the least soluble of these salts. If concentrated solutions of permanganate of potash and of nitrate of silver be mixed together, a red crystalline permanganate of silver

separates. It may be employed for the preparation of the other permanganates; if it be levigated with water, and mixed with a solution of the chloride of the metal, of which the permanganate is required, double decomposition occurs, and chloride of silver is formed, whilst the desired permanganate is obtained in solution. In this way the permanganate of baryta may be procured, and from it the permanganic acid may be obtained in solution, by the cautious addition of dilute sulphuric acid, as long as any precipitate is produced. On evaporation it may be obtained as a brown partially crystalline mass, which is very soluble in water; its solution is decomposed by mere elevation of the temperature; a little beyond  $100^{\circ}$  F. hydrated peroxide of manganese is deposited, and oxygen gas escapes.

(667) *Protosulphide of Manganese* is obtained as a yellowish red hydrate, by precipitating a salt of the protoxide by hydrosulphate of ammonia. It speedily becomes oxidized by exposure to the air. A native sulphide of manganese is occasionally met with of a brownish black or steel-grey colour and feeble metallic lustre. The other sulphides of manganese have not been accurately examined.

(668) *Chlorides of Manganese*.—Three chlorides of this metal may be obtained: a protochloride, a sesquichloride, and a perchloride ( $\text{Mn}_2\text{Cl}_7$ ): but there is some doubt as to the composition of the latter compound.

*Protochloride of Manganese*, ( $\text{MnCl} + 4 \text{ aq}$ ); *Eq.* 63 + 36.—This substance is obtained abundantly as a waste product in the preparation of chlorine by acting on the black oxide of the metal: the chlorine escapes, and the chloride of manganese is dissolved. If this solution be evaporated to dryness, re-dissolved in water, and subjected to a current of sulphuretted hydrogen to reduce the iron to the state of protoxide, the manganese may be obtained free from iron, nickel, and cobalt by suspending freshly precipitated sulphide of manganese in water, and adding it to the liquid as long as the fresh portions of sulphide become blackened; the manganese displaces the other metals from their solution, and they are precipitated as black hydrated sulphides: for example,  $\text{FeCl} + \text{HO}, \text{MnS} = \text{MnCl} + \text{HO}, \text{FeS}$ .

On evaporation the chloride of manganese crystallizes in a tabular form with 4 equivalents of water. It is of a delicate pink colour and slightly deliquescent; by heat an anhydrous chloride may be obtained, which is soluble in alcohol, and crystallizes with two equivalents of alcohol.

A *sesquichloride* may be obtained in solution by acting on the sesquioxide of manganese with cold hydrochloric acid: it is of a dark brown colour: it must be concentrated by evaporation in vacuo.

The *Perchloride*  $\text{Mn}_2\text{Cl}_7$ ? (Dumas,) is obtained as a greenish-yellow gas, which condenses at  $0^\circ$  F. to a greenish-brown liquid, by dissolving permanganate of potash in oil of vitriol and adding fused chloride of sodium in small portions at a time. The fumes in a moist air assume a purple colour from the formation of permanganic acid: water decomposes it instantly, forming a red solution of permanganic and hydrochloric acids. It is probable that this compound is an oxychloride of the metal, somewhat analogous to chlorochromic acid (657).

*Fluorides* of manganese, corresponding to each of these chlorides, have been formed. . .

(669) *Sulphate of Manganese* ( $\text{MnO}, \text{SO}_3, 5 \text{ aq}$ , *Eq.* 75.5 + 45), is obtained by dissolving the binoxide in sulphuric acid; it crystallizes below  $42^\circ$  with 7 equivalents of water; between  $45^\circ$  and  $68^\circ$  with 5 equivalents; between  $68^\circ$  and  $86^\circ$  with 4 equivalents of water (Brandes). It forms a double salt with sulphate of potash ( $\text{MnO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6 \text{ aq}$ ), which is isomorphous with the corresponding double sulphate of magnesia. The sesquisulphate of manganese forms a double salt with sulphate of potash, which crystallizes in octohedra ( $\text{KO}, \text{SO}_3 + \text{Mn}_2\text{O}_3, 3 \text{ SO}_3 + 24 \text{ aq}$ ), and corresponds in form and composition with common alum.

*Carbonate of Manganese* ( $\text{MnO}, \text{CO}_2$ ); *Eq.* 57.5.—The anhydrous carbonate forms the native *manganese spar*, and frequently accompanies spathic iron: the artificial carbonate may be obtained as a white hydrate  $2 (\text{MnO}, \text{CO}_2) + \text{H}_2\text{O}$ , on precipitating the chloride by an alkaline carbonate: it becomes brownish by drying.

(670) *CHARACTERS OF THE SALTS OF MANGANESE.*—The salts of this metal are of a delicate rose colour; they have an astringent taste. With *potash* and *soda* they yield a white precipitate of hydrated protoxide, which rapidly absorbs oxygen, and becomes brown by exposure to the air. *Ammonia* gives a similar precipitate, which is soluble in excess of the ammoniacal liquid, especially when it contains chloride of ammonium; the solution quickly absorbs oxygen, and deposits a brown hydrated peroxide of manganese. The *alkaline carbonates* give a white precipitate of carbonate of manganese, soluble in chloride of ammonium. With *hydrosulphate of ammonia* a characteristic flesh-coloured hydrated sulphide of manganese is formed, which becomes brown by exposure to the air. *Sulphuretted hydrogen* gives no precipitate in the solutions of manganese. *Ferrocyanide of potassium* gives a white precipitate; in neutral solutions *ferridcyanide of potassium* produces a brown precipitate. Mr. Crum has pointed out an



extremely delicate test of the presence of manganese in the reaction which occurs if a compound of manganese be mixed with dilute nitric acid, and a little peroxide of lead be added: on boiling the mixture, the red colour of permanganic acid is produced by a trace of manganese which is too small to be otherwise recognised. *Before the blowpipe*, when fused on platinum wire or foil, with a little carbonate of soda, the compounds of manganese give a very characteristic bluish-green opaque bead: a bead of borax becomes violet in the oxidizing flame, if manganese be present; the colour disappears in the reducing flame.

(671) *Estimation of Manganese, and Separation from the Alkalies.*—Manganese is generally estimated in analysis in the form of the red oxide of manganese, which contains 72.7 per cent. of the metal. For this purpose it is precipitated from a boiling solution of its salts by carbonate of potash or soda, and the precipitated carbonate is well washed and then heated to redness, by which carbonic acid is expelled, and the red oxide is produced by absorption of oxygen from the air.

*Separation of Manganese from the Alkaline Earths.*—The solution must be rendered nearly neutral, and hydrosulphate of ammonia must be added, which precipitates the manganese as sulphide: the sulphide must then be re-dissolved in hydrochloric acid, precipitated by carbonate of potash, and the manganese is estimated, after ignition, as red oxide. It is however apt thus to retain some portions of the earths. The oxide must therefore be again re-dissolved in hydrochloric acid; chloride of ammonium must be added, and then a mixture of ammonia and carbonate of ammonia in excess; the manganese will be held in solution; but if lime, baryta, or strontia be present, it will remain undissolved in the form of carbonate, which must be collected on a filter, weighed, and deducted from the result.

*Separation from Zinc and Cadmium.*—The solution is mixed with acetate of potash and free acetic acid, then sulphuretted hydrogen is transmitted; the zinc and cadmium precipitate as sulphides, and the manganese remains in solution. If zinc be absent, the addition of acetic acid and the acetate is unnecessary.

The separation of manganese from cobalt and nickel is attended with considerable difficulty. Ebelmen recommends that the mixed oxides, after they have been reduced by ignition, be heated to dull redness in a current of sulphuretted hydrogen, the current of gas being continued as long as any water is formed, and until the mixture has been allowed to cool completely; the metals are thus converted into sulphides. Dilute hydrochloric acid in the cold

dissolves the sulphide of manganese, but leaves the sulphides of cobalt and nickel unacted upon.

• *Separation from Iron, Chromium, Uranium, Alumina, and Glucina.*—This is readily effected by converting the iron into a persalt, and after largely diluting the solution with water, digesting it upon finely levigated carbonate of baryta. Manganese alone remains in the liquid, the other oxides being displaced by baryta. The excess of baryta is removed by sulphuric acid, and the manganese precipitated by carbonate of soda.

## CHAPTER XV.

GROUP V.—CERTAIN METALS WHICH FORM ACIDS WITH OXYGEN.

### § I. TIN.

*Symbol, Sn; Equivalent, 58.82; Specific Gravity, 7.292.*

(672) THIS beautiful metal is one of those which have been longest known to man, as it is mentioned in the Books of Moses. Tin, however, is met with in but few localities. Its only ore of importance is the deutoxide, or tin-stone, which occurs crystallized in prisms, isomorphous with those of titanate of iron. It is usually found in veins, running through primitive rocks, of porphyry, granite, or clay-slate, and is generally mingled with the sulphides and arsenides of copper and iron, and frequently also with wolfram. The most celebrated tin mines are those of Cornwall, which were worked previous to the Roman invasion; they furnish annually upwards of 3000 tons of the metal. The mines of Malacca also yield a very pure tin: the metal is likewise obtained to a smaller extent from Mexico. The tin veins in Cornwall are frequently associated with those of copper, and they run almost invariably east and west. The tin ore is often met with in alluvial soils, whither it has been carried from its original position by the action of water. In this case the ore occurs in detached, rounded masses, and is very pure, constituting what is termed *stream tin*. The position of the veins is frequently traced by following the stream towards its source, up to the point where the ore ceases to be found; a careful examination of the vicinity generally leads to the discovery of the vein.

(673) *Extraction of Metallic Tin.*—In order to extract the metal from the ore, it is subjected to a series of operations,

some of which are of a mechanical, and others of a chemical character. They may be classified thus:—

1. *Stamping and washing* to remove the earthy and lighter portions.

2. *Roasting*, to decompose the pyrites and get rid of the arsenic and sulphur.

3. *Washing*, to dissolve out sulphate of copper and carry off the oxide of iron.

4. *Reduction*, by which the tin is separated from the oxygen and the *gangue* or earthy matter.

5. *Refining*, or liquation, and *boiling* with green wood.

1. The purer portions of the ore are first picked out by hand; the residuc, consisting chiefly of tin-stone, with the earthy impurities of the matrix, mixed with arsenical copper and iron pyrites, passes to the stamping mill, where it is reduced to a coarse powder. This powder is then buddled and washed to remove the lighter impurities.

2. The heavier portion, however, still retains a considerable quantity of arsenical iron and copper pyrites. The next operation is intended to get rid of these substances; with this view the washed ore is roasted in a reverberatory furnace until the arsenic and a good deal of the sulphur are expelled, and the ore becomes converted into yellowish-brown powder; this process usually lasts about twelve hours. During this roasting, frequent stirring is necessary in order to expose fresh surfaces freely to the air. By this means the iron pyrites is decomposed, and is converted into sulphurous acid and peroxide of iron; the arsenic is expelled as arsenious acid, and the greater part of the sulphide of copper is converted into sulphate of copper; this conversion is completed by exposing the mass in a moistened state to the air for some days.

3. The sulphate of copper is then dissolved out by lixiviation; after which the principal part of the peroxide of iron, as it is much lighter than the oxide of tin, is got rid of by washing.

4. The washed ore is now ready for reduction.—In order to attain this object it is mixed with from one-fifth to one-eighth of its weight of powdered anthracite or of charcoal, and with a small proportion of lime to facilitate the fusion of the siliceous gangue, which still remains mingled with the ore. The mixture having been rendered damp, for the purpose of preventing the finer particles from being carried away by the current of air, is introduced into the reducing furnace. This is a reverberatory furnace with a low arch or crown. The charge having been placed upon the hearth, the doors are closed up and the heat is gradually raised for

five or six hours; the oxide of tin is thus reduced by the carbon, before the temperature rises high enough to cause the oxide to fuse with the silica, with which it would form an enamel difficult of reduction. Towards the end of the operation the heat is raised until it becomes very intense, the slags are thus rendered fluid, and the reduced metal subsides to the bottom and is allowed to run off into cast-iron pans, from which it is ladled off into moulds; but the ingots thus obtained are by no means pure.

5. They are therefore next submitted to a process of *liquation*, which consists in heating the ingots to incipient fusion, upon the bed of a reverberatory furnace: the purer tin being the more fusible portion, gradually melts out and leaves an alloy which has a higher melting point. This less fusible portion when remelted forms the inferior variety called *block tin*. The tin which has run out of the ingots is drawn off into a second pan in which the metal is gently heated, being kept in a state of fusion by a fire underneath; here it is agitated briskly by thrusting into the mass stakes soaked in water; the steam thus produced, as it bubbles up through the molten metal, carries the dust, slag, and other mechanical impurities to the surface. After this treatment has been continued for about three hours, the metal is allowed to remain undisturbed for a couple of hours; it is then skimmed, ladled out and cast into ingots for the market. The portion contained in the upper half of the pan is the purest, as owing to the low density of tin, and its tendency to separate from its alloys, it rises to the surface. The finest quality of the metal is frequently heated a second time to a temperature a little short of its melting point; at this high temperature it becomes brittle, and, if allowed to fall from a height, it breaks into irregular prismatic fragments, which are known as *dropped* or *grain tin*. The splitting of the mass into these fragments is a rude guarantee of the purity of the metal, since impure tin does not become brittle in this manner.

On the continent the stream tin is frequently reduced in small blast furnaces termed by the French *fourneaux à manche*; the fuel used in this case is charcoal. The tin which is imported from Banca is almost chemically pure. English tin usually contains small quantities of arsenic, of copper, of iron, and of lead.

When required in a state of perfect purity, the metal may be obtained by means of voltaic action. For this purpose a concentrated solution of crude tin in hydrochloric acid is placed in a beaker, and water is cautiously poured in without disturbing the dense solution below. If a bar of tin be plunged into the

liquid, beautiful prismatic crystals of pure tin are gradually deposited on the bar at the point of junction between the metallic solution and the water.

(674) *Properties.*—Tin is a white metal with a tinge of yellow, and has a high metallic lustre. It is rather soft, and is very malleable, but is deficient in tenacity. At a temperature of about  $212^{\circ}$  its ductility is considerable, and it may then be easily drawn into wire. In a laminated state it is well known as *tin foil*. If a bar of tin be bent, it emits a creaking sound, a property which it possesses in common with cadmium; if bent several times in succession backwards and forwards, it becomes sensibly hot at the point of flexure. These effects depend upon a mechanical alteration of the relative position of its molecules, and their mutual friction. Tin, when handled, communicates a peculiar odour to the fingers. Tin is a tolerably good conductor both of heat and electricity. It fuses at  $442^{\circ}$  F., but it is not sensibly volatilized in the furnace. It may be obtained in crystals by slow cooling. Tin is but slowly tarnished by exposure to the air and moisture at ordinary temperatures, but if exposed to the air at a high temperature it becomes rapidly oxidized and burns with a brilliant white light. Nitric acid acts upon it violently, and produces an insoluble hydrated binocide of the metal; at the same time, owing to the decomposition of water, a considerable quantity of ammonia is formed, which enters into combination with the excess of acid. Strong hydrochloric acid when heated upon tin, dissolves it gradually with extrication of hydrogen. Dilute sulphuric acid is without action on the metal; but if the concentrated acid be boiled upon it, the tin becomes converted into sulphate, while sulphurous acid escapes.

Owing to its brilliancy, and its power of resisting ordinary atmospheric changes, tin is largely employed as a coating upon other more abundant, but more oxidizable metals, to protect them during use. Iron and copper are especially adapted to the operation of tinning. In India, tin is applied instead of silver to steel and iron articles by way of ornament; the tin is melted, and while still liquid is agitated in a box till it has become solid; the fine powder thus procured is separated, by suspension in water, from the coarser particles, and is made into a thin paste with glue; it is then applied in the desired pattern; when perfectly dry it is burnished and varnished; its brilliancy is thus preserved unchanged.

(675) *Tin Plate.*—The ordinary process of tinning differs from the foregoing one, and is far more important in its economical

results. In tin plate an actual alloy of the two metals is formed upon the surface of the iron, the external surface being pure tin. For the manufacture of tin plate, the best charcoal iron is required. After the iron has been rolled and cut into sheets of suitable thickness and size, its surface is made chemically clean. For this purpose the sheets are immersed for four or five minutes in a mixture of sulphuric acid and water; after which they are raised to a red heat in a reverberatory furnace; they are then withdrawn, allowed to cool, and hammered flat. In order to detach from them all the scales of oxide, they are passed between polished rollers, and as they emerge they are plunged one by one into a mixture of bran and water which has become sour by exposure to the air; here they remain for some hours, and are thence transferred to a vessel containing a mixture of dilute sulphuric and hydrochloric acids; lastly, they are scoured with bran, and plunged into pure water or lime water, where, if the surface be clean on immersion, they may remain for any length of time without rusting: these preliminary steps are necessary in order to secure a clean surface, as the tin will not adhere to an oxidated or even a dusty plate. More recently, the plates after scouring have been cleaned with hydrochloric acid holding zinc in solution, and then dipped into the melted tin in the manner about to be described.

In order to tin them they are plunged one by one into a large vessel of melted tallow free from salt, and after remaining there for an hour they are immersed in the bath of melted tin, which is preserved from oxidation by a stratum of grease three or four inches thick. Here they remain for about an hour and a half, they are then withdrawn and allowed to drain. After this they are plunged into a second bath of pure tin, and the superfluous tin is removed by again heating them in a bath of tallow; the tin melts and runs down to the lower edge of the plate; when cool, this thickened margin is finally reduced by dipping the edge of the plate once more into melted tin, the heat of which quickly fuses the superfluous metal, which is then detached by giving the plate a sharp blow. Tin plate is sometimes made to exhibit a beautiful crystalline appearance, known under the term *moirée métallique*. A mixture of 2 parts of nitric acid, with 2 of hydrochloric acid, is made with 4 of water: the tin plate is gently heated and the liquid spread evenly over with a sponge; the crystals gradually appear. The plate is then plunged into water, dried quickly, and varnished. Different coloured varnishes are used to vary the effects.

Tinning of copper is the same in principle, but is a simpler

operation than the tinning of iron: the surface of the metal is rendered clean by rubbing it while heated with sal ammoniac; when quite bright the copper is sprinkled with a little rosin to prevent oxidation, and melted tin is then poured on, and spread over the surface with tow by the workman, who keeps the article constantly at a high temperature; the superfluous tin is wiped off with the tow. The addition to the tin of one-fourth of its weight of lead renders the operation more easy, as the alloy is more perfectly liquefied.

(676) The alloys of tin which are employed in the arts are numerous. *Britannia Metal* is one which is a good deal used for making teapots and spoons of a low price; it consists of equal parts of brass, tin, antimony, and bismuth. *Pewter* is another alloy of this description; both of these possess considerable malleability, pewter being intermediate in hardness between lead and Britannia metal. The best pewter consists of 4 parts of tin, and 1 of lead. Another alloy, which is intermediate in properties between pewter and Britannia metal, is called *Queen's metal*; it is used for the manufacture of teapots and common spoons. It consists of 9 parts of tin, 1 part of antimony, 1 of bismuth, and 1 of lead.

*Plumber's solder* is an alloy of tin and lead which is more fusible than pure lead. *Fine solder* consists of 2 parts tin and 1 of lead; *common solder* of equal parts of lead and tin; and *coarse solder* is composed of 2 of lead to 1 of tin.

Tin forms several very useful alloys with copper. *Bell metal* consists of about 78 of copper and 22 of tin, or ( $\text{Cu}_8\text{Sn}$ ). *Gun metal* contains 9 or 10 per cent. of tin. *Bronze* contains less tin, with usually an addition of 3 or 4 per cent. of zinc. Bronze admits of a peculiar kind of tempering. If it be annealed, and allowed to cool slowly, it becomes hard, brittle, and elastic; but if cooled suddenly, it may be hammered, and worked at the lathe; this property is taken advantage of in the manufacture of articles with this alloy; they are wrought in the soft state, and are afterwards hardened by annealing. The effect of sudden cooling upon bronze is therefore just the reverse of that which is produced by it upon steel. These alloys of copper and tin are much harder than copper itself, and considerably more fusible. The melting point of copper, according to Daniell, is  $1996^\circ$ , but an alloy of tin and copper containing 6.6 per cent. of tin, fused at  $1690^\circ$ ; and one with 12.3 per cent. of tin, at  $1534^\circ \text{F}$ . These alloys have a specific gravity greater than the mean of the metals which enter into their composition. They resist oxidation in the air more completely than copper.

An inconvenience in the use of the alloys of copper and tin

arises from the circumstance, that, when melted, the two metals, owing to their difference in density, have a tendency to separate from each other, even after they have been well incorporated: the tin accumulates in the upper portions of the melted mass, where it forms a more fusible alloy. It is therefore very difficult in large castings to obtain a mass of metal the composition of which is uniform throughout.

*Speculum Metal*, used for the mirrors of reflecting telescopes, consists of 1 part tin and 2 copper, or ( $\text{SnCu}_2$ ). It is of a steel white colour, extremely hard, brittle, and susceptible of a high polish.

The *Amalgam of Tin and Mercury* is employed for the silvering of mirrors. In order to apply it to the glass, a sheet of tinfoil is spread evenly upon a smooth slab of stone, which forms the top of a table carefully levelled and surrounded by a groove, for the reception of the superfluous mercury. Clean mercury is poured upon the tinfoil, and spread uniformly over it with a roll of flannel; more mercury is then poured on until it forms a fluid layer of the thickness of about half-a-crown; the surface is cleared of impurities by passing a linen cloth lightly over it, the plate of glass is carefully dried, and its edge being made to dip below the surface of the mercury, is pushed forward cautiously; all bubbles of air are thus excluded as it glides over and adheres to the surface of the amalgam. Weights are then placed upon the glass, and the stone is gently inclined so as to allow the excess of mercury to drain off; the plate is then covered with flannel and loaded with weights for 24 hours, at the end of which time it is placed upon a wooden table, the inclination of which is increased from day to day until the mirror assumes a vertical position: in about a month it is sufficiently drained. The amalgam usually contains about 4 parts of tin to 1 of mercury.

Several of the compounds of tin are employed in the arts. The binoxide is used to some extent in the preparation of enamels, and both the chlorides of tin are substances of great importance to the dyer and the calico printer.

(677) *Oxides of Tin*.—With oxygen, tin forms two principal compounds, the protoxide and the binoxide, besides some intermediate oxides of minor importance.

*Protoxide of Tin* ( $\text{SnO}$ , Eq. 67), is obtained as a white hydrate, ( $\text{SnO}, \text{HO}$ ), by pouring a solution of the protochloride of the metal into one of carbonate of soda or potash in excess; the carbonic acid escapes with effervescence. When moist, this hydrate absorbs oxygen



from the air, but not when dry. By ignition in close vessels filled with nitrogen or with carbonic acid it becomes anhydrous. If heated in the open air it glows, and is converted into the binoxide. If the hydrated oxide be boiled with a solution of potash in excess, it is dissolved, and in a few days metallic tin separates, peroxide of the metal remaining in solution. If boiled with a weak solution of potash, in quantity insufficient to dissolve the oxide, it becomes anhydrous, and is converted into a mass of black crystalline needles; these needles when heated decrepitate powerfully, increase in bulk, and are converted into an olive-brown powder. The oxide may also be procured of a brilliant scarlet colour, which however by friction disappears, and becomes brown. The hydrated oxide is readily dissolved by acids, but the anhydrous oxide is more slowly acted upon.

(678) *Binoxide of Tin* ( $\text{SnO}_2$ , *Eq.* 75; *Sp. Gr.* 6.95), occurs native in the anhydrous form, and constitutes the only ore of tin that is worked. It is met with crystallized in square prisms, which have usually a brown colour, owing to the presence of oxide of iron. It is insoluble in acids, but if heated with an alkali, it enters into combination with it, and forms a soluble compound.

In its hydrated condition binoxide of tin has the characters of an acid, and forms two remarkable varieties, which have been termed metastannic and stannic acid (*Freymy, Ann. de Chimie*, III. xxiii. 393). Like the metaphosphoric and phosphoric acids, they require each a different amount of base for saturation, the stannic acid combining with the greatest proportion of base.

*Metastannic Acid*, ( $\text{Sn}_5\text{O}_{10}$ ), is readily procured by treating metallic tin with nitric acid; violent action, attended with extrication of nitrous fumes, occurs, and the tin is converted into a white crystalline insoluble mass, which is hydrated metastannic acid; after washing it with cold water, the acid, when dried in air, consists of  $\text{Sn}_5\text{O}_{10} + 10 \text{HO}$  (*Freymy*). In this state it reddens litmus paper; when dried at  $212^\circ$  it loses half its water, and by ignition becomes anhydrous, and of a pale buff colour: in this form it possesses the properties of the native oxide, and constitutes the *putty powder* employed for polishing plate; it is also largely used for giving whiteness and opacity to enamels.

In its hydrated form metastannic acid is insoluble in nitric acid; concentrated sulphuric acid, when heated with it, dissolves it freely and forms a compound soluble both in water and in alcohol; by boiling the solution it is decomposed, and the two acids are separated. Hydrochloric acid combines with it, but does not dissolve it; the compound is soluble in pure water, but is reprecipitated

on the addition of acid in excess, or on boiling the solution. Metastannic acid is freely soluble in solutions of potash and soda, as well as in solutions of their carbonates, but it is not dissolved by ammonia. These metastannates are not crystallizable, and are precipitated by adding caustic potash to the aqueous solution; the granular precipitate may be drained upon a tile, and dried at  $260^{\circ}\text{F}$ . The potash salt has a strongly alkaline reaction; it consists of  $(\text{KO}, \text{Sn}_5\text{O}_{10}, 4 \text{ aq})$ . The metastannates of the alkalis, when strongly heated, are decomposed and become insoluble; when treated with water, metastannic acid is left, whilst the alkali is dissolved. Metastannic acid may be recognised by the beautiful golden-yellow colour which it yields when its hydrate is moistened with protochloride of tin, owing to the formation of metastannate of tin,  $(\text{SnO}, \text{Sn}_5\text{O}_{10}, 4 \text{ aq})$ . The only metastannates which are soluble are those of potash and soda; they are precipitated in the gelatinous state from their solutions by the addition of almost any of the neutral salts of soda, potash, or ammonia.

(679) *Stannic Acid*,  $(\text{HO}, \text{SnO}_2)$ .—This variety of the hydrated oxide of tin may be procured by precipitating a solution of bichloride of tin by ammonia, or still better by an insoluble carbonate, such as chalk or carbonate of baryta, when it separates as a gelatinous precipitate which may be readily washed clean: when dried in vacuo, the composition of the hydrate is  $(\text{HO}, \text{SnO}_2)$ . In this state it is freely soluble in hydrochloric acid, with which it reproduces bichloride of tin; it is also soluble even in dilute sulphuric acid, but the stannic acid is separated on boiling. Nitric acid dissolves it freely. Stannic acid is soluble in the cold in solutions of potash and of soda, but not in ammonia; by a heat of  $284^{\circ}\text{F}$ . it is converted into metastannic acid. In combination with the alkalis it forms compounds which crystallize readily, especially from solutions which contain an excess of alkali.

*Stannate of Potash*,  $(\text{KO}, \text{SnO}_2, 4 \text{ HO})$ , is easily prepared by heating any form of peroxide of tin with excess of caustic potash; on dissolving and evaporating the product, crystals are formed. When heated to redness, the stannate of potash may be rendered anhydrous. The soluble stannates have a powerful alkaline reaction; they absorb carbonic acid from the air when in solution, and are precipitated by solutions of most of the salts of potash, soda, and ammonia.

*Stannate of Soda*,  $(\text{NaO}, \text{SnO}_2 + 4 \text{ aq})$ , may be prepared in the same way as the stannate of potash. It crystallizes with facility in six-sided tables, when a solution saturated at about  $100^{\circ}\text{F}$ . is heated

to the boiling point, as it is more soluble in cold than in hot water. This stannate is now largely prepared as a mordant for the use of the dyer and calico-printer. It forms the basis of what is technically known as *tin prepare liquor*. Copper is quickly tinned by a solution of this salt.

*Stannate of the Protoxide of Tin*, ( $\text{SnO}, \text{SnO}_2$ ), may be prepared as a slimy grey hydrate, soluble in ammonia, by boiling pure hydrated sesquioxide of iron with a solution of protochloride of tin. It is soluble in hydrochloric acid; the solution gives a purple precipitate with salts of gold.

(680) The *Sulphides of Tin* are three in number,—the protosulphide, the bisulphide, and the sesquisulphide: the latter is unimportant.

The *Protosulphide of Tin*, ( $\text{SnS}$ ), *Eq. 75*, may be formed by fusing the metal with sulphur, when it forms a bluish grey crystalline mass, easily dissolved by melted tin; it may also be obtained by passing sulphuretted hydrogen through a protosalt of tin in solution, when it falls as a chocolate-brown hydrate. It is soluble in sulphide of ammonium, and in the alkaline sulphides, if they contain an excess of sulphur. Protosulphide of tin combines with the sulphides of the electro-negative metals, such as arsenic and antimony. It is also dissolved by hydrochloric acid with extrication of sulphuretted hydrogen. The *sesquisulphide* ( $\text{Sn}_2\text{S}_3$ ) may be prepared by mixing the protosulphide with one-third its weight of sulphur, and heating to dull redness; it is only partially soluble in hydrochloric acid.

The *Bisulphide of Tin*, ( $\text{SnS}_2$ , *Eq. 91*), is known as *Mosaic gold*; it forms a beautiful yellow flaky compound, which is obtained by preparing an amalgam of 12 parts of tin and 6 of mercury: this is reduced to powder and mixed with 7 parts of sublimed sulphur and 6 of sal ammoniac. This mixture is introduced into a flask with a long neck, and is heated gently as long as a smell of sulphuretted hydrogen is perceptible; the temperature is then raised to low redness; calomel and cinabar are sublimed, and a scaly mass of bisulphide of tin remains. If the heat be pushed too far, part of the sulphur is expelled, and the operation fails. The sal ammoniac appears by its volatilization to moderate the heat produced during the sulphuration of the tin, which would otherwise rise so high as to decompose the bisulphide. Bisulphide of tin is used in the arts to imitate bronze. Aqua regia is the only acid that decomposes it, but it is readily soluble in the alkalis. A hydrated bisulphide of tin, of a dingy yellow, is produced by passing sul-

phuretted hydrogen through a solution of the persalts of tin. This hydrate is readily dissolved by sulphide of ammonium, evolving sulphuretted hydrogen: it is also soluble in the alkalies, and in hot hydrochloric acid. With sulphide of sodium it forms a salt which may be obtained in yellow crystals of  $2 \text{ NaS}, \text{SnS}_2 + 12 \text{ aq.}$

The bisulphide fuses when chlorine is passed over it; 6 equivalents of the gas are absorbed, and a yellow crystalline compound is obtained without the aid of heat, which may be considered as a compound of 1 equivalent of bichloride of tin with 2 equivalents of bichloride of sulphur,  $\text{SnCl}_2, 2 \text{ SCl}_2$ .

(681) CHLORIDES OF TIN.—Tin forms with chlorine two compounds, which correspond in composition with the sulphides of the metal.

*Protochloride of Tin*, ( $\text{SnCl}$ ); *Eq.* 94.5.—The hydrate of this salt may be obtained by dissolving tin in hydrochloric acid. This solution is usually effected on the large scale in copper vessels, since the voltaic opposition of the two metals favours the solution of the tin: on evaporating the liquid till it crystallizes, prismatic needles are formed ( $\text{SnCl}, 2 \text{ aq.}$ ; *sp. gr.* 2.759); by a heat of  $212^\circ$  it may be rendered anhydrous, but it generally loses a portion of hydrochloric acid at the same time. The protochloride is decomposed if mixed with a large quantity of water, hydrochloric acid remains in solution, and a white, hydrated oxychloride,  $\text{SnCl}, \text{SnO}, 2 \text{ aq.}$  subsides. When exposed to the air, either in crystals or in solution, it absorbs oxygen and forms a mixture of bichloride and oxychloride of tin. Protochloride of tin has a powerful affinity both for chlorine and for oxygen; it therefore acts as a powerful reducing agent. Thus it deoxidizes completely the salts of mercury, of silver, of gold, of antimony, and of arsenic. Advantage is sometimes taken of this circumstance in the analytical determination of the quantity of mercury, since all the salts of mercury, when boiled with the protochloride of tin, are decomposed, and yield their mercury in a metallic form. Sulphurous acid is likewise deprived by it of its oxygen, and it consequently produces a precipitate of sulphide of tin when mixed with a solution of the salt. It reduces the metallic acids in the salts of chromic, tungstic, molybdic, and manganic acids to a lower state of oxidation; and converts the persalts of iron into protosalts, and the protosalts of copper into salts of the red oxide. Protochloride of tin is extensively employed as a mordant by the dyer and calico printer, under the name of *salts of tin*, and they also use it for deoxidizing indigo and the peroxides of iron and manganese. It forms double chlorides with many

of the chlorides of the metals of the alkalis and alkaline earths; these double salts are capable of crystallization. The protochloride or *butter of tin* may be procured in the anhydrous form<sup>a</sup> by distilling a mixture of equal weights of tin filings and corrosive sublimate;  $\text{HgCl} + \text{Sn} = \text{SnCl} + \text{Hg}$ : it remains behind as a grey brilliant mass with a vitreous fracture; at a full red heat it may be distilled. On passing a current of chlorine over it, heat and light are evolved, and the bichloride of tin is formed.

(682) *Bichloride of Tin*,  $(\text{SnCl}_2)$ , *Eq.* 130.—This compound may be prepared also by passing dry chlorine over melted tin, or else by mixing 4 parts of corrosive sublimate with 1 part of tin filings: on the application of heat a colourless liquid distils, which was formerly known as the *liquor fumans Libavii*;  $2 \text{HgCl} + \text{Sn} = \text{SnCl}_2 + \text{Hg}$ . It emits dense white fumes when exposed to the air, and has a sp. gr. of 2.28: it boils at  $248^\circ \text{F.}$ , and gives off a vapour of a density of 9.2. When mixed with water, intense heat is evolved, and a hydrate is formed; this compound crystallizes in rhombs  $(\text{SnCl}_2, 2 \text{aq})$ , when it is allowed to form spontaneously, by attracting moisture from the air: but though freely soluble in a small quantity of water, copious dilution causes the precipitation of hydrated stannic acid, and hydrochloric acid is set free. Bichloride of tin is readily soluble in water acidulated with hydrochloric acid. The bichloride of tin forms numerous double salts with the soluble chlorides; the compound with chloride of potassium crystallizes in anhydrous octohedra,  $\text{KCl}, \text{SnCl}_2$ ; a similar constitution holds in the corresponding ammoniacal salt,  $\text{NH}_4\text{Cl}, \text{SnCl}_2$ , which is the *pink salt* of the dyer. An impure bichloride of tin is largely used by the dyers under the name of nitromuriate of tin, or *composition*; it is generally prepared by dissolving tin at a gentle heat in a mixture of nitric acid and sal ammoniac. The other salts of tin are unimportant.

(683) *CHARACTERS OF THE SALTS OF TIN*.—Tin forms two series of salts, the salts of the protoxide and the salts of the peroxide: the bichloride of tin is the only salt of the latter class that has been minutely examined.

1. The *Protosalts of Tin* are nearly colourless; they have a powerful styptic taste; when in solution they absorb oxygen rapidly from the air; when largely diluted with water the solution becomes milky, but it is rendered clear by a small excess of hydrochloric acid. The *fixed alkalies* produce a white precipitate of hydrated protoxide of tin, which is soluble in excess of the alkali, but on boiling, part of the tin is deposited as a black metallic powder.

*Ammonia* gives a white hydrated oxide of tin, but the precipitate is not redissolved by an excess of ammonia. The *alkaline carbonates* give a similar precipitate, whilst carbonic acid escapes with effervescence. A very characteristic reaction is the production, with *sulphuretted hydrogen*, of a chocolate-brown precipitate of hydrated protosulphide of tin. With *sulphide of ammonium*, a similar precipitate is formed, which is soluble in the alkaline sulphides. With dilute solution of *chloride of gold*, they give, if used in excess, a brown precipitate of reduced gold; in smaller quantity, they yield a beautiful purple precipitate, the purple of Cassius. *Ferrocyanide of potassium* gives a white precipitate, soluble in hydrochloric acid.

2. The *Persalts of Tin* are found to give with the *caustic alkalies* a white precipitate, soluble in excess of the alkalies; it is not precipitated on boiling the solution. *Carbonates of the alkalies* give a white hydrated oxide with escape of carbonic acid: the precipitate is insoluble in excess of the alkaline salt. *Sulphuretted hydrogen* and *hydrosulphate of ammonia* both produce a dirty yellow precipitate of hydrated sulphide of tin, which is soluble in excess of the alkaline sulphides, and in the caustic alkalies. All the compounds of tin *before the blowpipe* with soda on charcoal in the reducing flame, give white malleable globules of the reduced metal.

(684) *Estimation of Tin, and separation from the foregoing Metals.*—Tin is estimated in the form of the anhydrous peroxide; 100 parts of which contain 78·66 of the metal.

The separation of tin from all the metals hitherto described, is effected by means of sulphuretted hydrogen. With the exception of cadmium, none of these metals is precipitated by the gas. The mixed sulphides of tin and cadmium may be at once evaporated to dryness with nitric acid: on treating the residue with water, nitrate of cadmium will be dissolved, and the insoluble oxide of tin will remain. The sulphide of cadmium is also easily separated from the sulphides of tin by hydrosulphate of ammonia, which dissolves the sulphides of tin and leaves the sulphide of cadmium. Both the sulphides of tin, by ignition in a current of air, are gradually converted into the binoxide of tin: this change may be accelerated by moistening them with nitric acid.

Tin may also be separated from all metals, with the exception of antimony, arsenic (and lead if sulphuric acid be present), by evaporating the solution nearly to dryness with nitric acid, and washing the residue with water strongly acidulated with nitric acid. The tin remains as metastannic acid, and by ignition furnishes the anhydrous peroxide.

## § II. TITANIUM.

*Symbol, Ti; Equivalent, 24.12?*

(685) TITANIUM is a comparatively rare metal, which presents considerable analogy with tin. Its principal ores are titaniferous iron, and rutile, anatase, or brookite, which are three different forms of titanic acid,  $\text{TiO}_2$ , coloured by variable quantities of the oxides of iron, manganese, and chrome. When titanic acid is intensely heated with charcoal, it is reduced, but is not fused. A remarkable compound of the metal is frequently found, in the form of copper-coloured cubic crystals, adhering to the slags of the Welsh iron furnaces. These crystals are hard enough to scratch agate; they have a sp. gr. of 5.3. No acid, except a mixture of nitric and hydrofluoric acids, has any action upon them, but they are oxidized by fusion with nitre, or by ignition in a current of oxygen. These crystals were supposed by Wollaston to be metallic titanium, but Wöhler showed that they consist of a combination of cyanide with nitride of titanium; they contain 18 per cent. of nitrogen, and 4 of carbon, having a formula  $\text{TiCy} + 3(\text{Ti}_3\text{N})$ . Another nitride of the metal,  $\text{Ti}_3\text{N}_2$ , also formerly mistaken for metallic titanium, is procured in copper-coloured scales by igniting the ammonio-chloride of titanium ( $2 \text{H}_3\text{N}, \text{TiCl}_2$ ) in close vessels, in a current of ammonia. Pure titanium may be obtained by decomposing the double fluoride of titanium and potassium with potassium. It then forms a grey amorphous powder, which burns in air with scintillation, and deflagrates in oxygen with dazzling brilliancy.

(686) Three *Oxides of Titanium* probably exist—the protoxide, the sesquioxide, and the deutoxide or titanic acid.

The *Protoxide* ( $\text{TiO}$ , *Eq.* 32), has not been obtained in a pure state. It appears to be formed when titanic acid is heated in a crucible lined with charcoal: but where the acid is actually in contact with the charcoal, a film of metallic titanium is formed. The protoxide is a black powder nearly insoluble in acids, and is gradually oxidized by exposure to a high temperature in air, or by fusion with nitre.

If a solution of titanic acid in hydrochloric acid be digested with zinc, a purple hydrated *sesquioxide* of titanium is deposited, which absorbs oxygen from the air with great rapidity, becoming white from the formation of titanic acid. Hydrochloric acid dissolves it sparingly, and forms a blue solution.

*Titanic Acid* ( $\text{TiO}_2$ ), *Eq.* 40.—This compound occurs in *menaccanite* and *iserine* as titanate of iron; but more commonly it is met with in the uncombined condition, constituting the principal

ore of the metal. It is found native under three distinct crystalline forms, each of which has a different specific gravity. Of these, the densest and most abundant is *rutile*, of specific gravity 4.25: it occurs in long striated prisms or needles of a brown colour, isomorphous with those of tin-stone. The second variety, *brookite*, of specific gravity 4.13, is found in right rhombic prisms, sometimes opaque, at others transparent, and of a pale brown; whilst the third variety, *anatase*, is found at Dauphiny in acute octohedra, which are semitransparent and of a yellowish brown or blue colour; they have a specific gravity of 3.9. Corresponding differences are observed in the titanic acid artificially prepared in the laboratory. Like the oxide of tin, it may be obtained in two isomeric forms, possessed of different properties. In fact, the existence of two dissimilar modifications is a very usual occurrence in the case of metallic oxides possessed of feeble acid powers.

Pure titanic acid may be obtained by reducing rutile to a fine powder, and fusing it with thrice its weight of carbonate of potash. On treating the mass with hot water, an impure bititanate of potash remains. It is dissolved in hydrochloric acid, next mixed with an excess of ammonia, and the precipitate is digested in hydrosulphate of ammonia, by which the tin, iron, and manganese are converted into sulphides, whilst the titanic acid remains unchanged: a solution of sulphurous acid then dissolves the sulphides, and a pure white titanic acid is left. By long continued ignition, the colour of this white acid deepens, and its specific gravity increases till it acquires a density equal to that of rutile. In this state it is insoluble either in solutions of the alkalis, or in acids, except hydrofluoric acid, or in boiling oil of vitriol. This modification of the acid may however be converted into the soluble form, by heating it with a fixed alkaline carbonate, then dissolving the residue with cold hydrochloric acid, and precipitating the titanic acid by means of carbonate of ammonia: it thus forms a white gelatinous hydrate, which dries into a semitransparent mass capable of reddening litmus. The liquid long remains turbid; it cannot be rendered clear by filtration, unless an excess of some ammoniacal salt be present. Hydrated titanic acid is dissolved by the alkalis in solution, and it yields definite salts with them. When fused with potash it forms a transparent yellowish glass. The hydrate of titanic acid is soluble in dilute hydrochloric acid; it is also dissolved by sulphuric acid, and forms a definite sulphate ( $\text{TiO}_2, \text{SO}_3$ ), which may be evaporated to dryness at a low temperature without undergoing decomposition. Both these acid solutions are decomposed by boiling them; and the



insoluble variety of titanic acid is precipitated. When heated it loses water and becomes insoluble. It becomes yellow on ignition, but recovers its whiteness on cooling.

(687) A *Bisulphide of Titanium* ( $\text{TiS}_2$ ), may be obtained in green scales; it is not soluble in the alkaline sulphides.

*Bichloride of Titanium* ( $\text{TiCl}_2$ , *Eq.* 95), is a fuming volatile liquid, resembling the bichloride of tin. It may be obtained by decomposing pure titanic acid, intimately mixed with charcoal, and heated to redness in a porcelain tube, by means of a current of dry chlorine gas. It is a colourless liquid, which boils at  $277^\circ \text{F.}$ , and yields a vapour of sp. gr. 6.836; with a small quantity of water it combines to form a crystallizable compound. A large quantity of water produces its decomposition, hydrated titanic acid being separated.

(688) CHARACTERS OF THE COMPOUNDS OF TITANIUM.—The salts of the protoxide are little known; with the *alkaline carbonates* they give a blue precipitate, which becomes first brown and ultimately green. The titanates of the alkalis are of a yellowish white colour; if neutral, they are insoluble; hot water removes the alkali, while most of the titanic acid remains undissolved. Hydrochloric acid dissolves them, forming a solution, which, when boiled, becomes turbid from deposition of titanic acid; *ammonia*, when added to this solution, produces a white precipitate. *Infusion of galls* produces an orange coloured precipitate in the acid solutions of the titanates; a precipitate of similar colour is produced by *ferrocyanide of potassium*. In the reducing flame of the *blowpipe* the titanates give with microcosmic salt a beautiful purple or bluish glass, which becomes colourless in the oxidizing flame. This reaction distinguishes the titanates from the tantalates.

(689) *Estimation of Titanium*.—Titanium is always estimated in the form of titanic acid. Its solution in cold hydrochloric acid is not precipitated by sulphuretted hydrogen, by which means it may be separated from tin and cadmium, both of which are thrown down as insoluble sulphides. The solution is then mixed with tartaric acid, and supersaturated with hydrosulphate of ammonia. Iron, nickel, cobalt, manganese, and zinc are thus separated in the form of sulphides. The solution is then evaporated to dryness, and the carbon is burned off; titanic acid is left, mixed with the earthy and alkaline salts of the mixture; the residue is fused with potash, redissolved in the cold with hydrochloric acid, and on boiling the liquid, to which a little dilute sulphuric acid has been added, the

titanic acid is precipitated. This process, however, is not very accurate; indeed the exact determination of the quantity of titanium in its compounds is a matter of considerable difficulty.

### § III. COLUMBIUM, NIOBIUM, ILMENIUM.

(690) COLUMBIUM or *tantalum* occurs in the tantalite of Bohemia, and *niobium* is a metal found by H. Rose in the American tantalite. These metals have been as yet but imperfectly studied, and are too rare to need a detailed notice here; they have a considerable analogy with silicon. According to M. Hermann the ytthro-tantalite of Siberia contains a new metal analogous to columbium, to which he has given the name of *ilmenyum*.

### § IV. MOLYBDENUM.

*Symbol*, Mo; *Equivalent*, 46.0; *Specific Gravity*, 8.615 to 8.636

(691) The principal ore of molybdenum is the bisulphide, a mineral in appearance much resembling plumbago, and which occurs chiefly in Bohemia and in Sweden. Molybdenum is also occasionally found oxidized, in combination with oxide of lead as molybdate of lead. The metal may be obtained by roasting the pure native sulphide in a free current of air; the sulphur passes off as sulphurous acid, whilst the molybdenum also combines with oxygen, and remains behind in the form of molybdic acid. If this be mixed into a paste with oil and charcoal, and exposed to the heat of a smith's forge, in a crucible lined with charcoal, it is reduced to the metallic state. In this form molybdenum is white, brittle, and very difficult of fusion. The acid may also be reduced by heating it to redness in a porcelain tube in a current of hydrogen: when the pulverulent metal is heated in the open air it is gradually oxidized, and finally converted into molybdic acid. It is also oxidized by nitric acid; if the metal be in excess, a soluble nitrate of the binoxide is obtained; if the acid predominate the oxidation proceeds further, and molybdic acid is formed; aqua regia produces similar results. Molybdenum is also oxidized when fused with nitre, and molybdate of potash is produced.

(691 *bis*) *Oxides of Molybdenum*.—Molybdenum forms 3 oxides; the protoxide (MoO), and the deutoxide (MoO<sub>2</sub>) are both possessed of basic characters: the third (MoO<sub>3</sub>) is a powerful metallic acid.

The *protoxide* (MoO, *eq.* 54,) is precipitated as a black hydrate from the protochloride by means of ammonia; it is soluble in

solutions of carbonate of ammonia, but not in those of the fixed alkalies or their carbonates. It may also be obtained in the anhydrous form, by digesting molybdic acid with zinc and hydrochloric acid.

The *deutoxide* ( $\text{MoO}_2$ ), *eq.* 62,) may be prepared by igniting a mixture of 2 parts of molybdate of soda and 1 part of sal ammoniac, and digesting the mass in solution of potash, to remove any undecomposed molybdic acid. The residue when well washed is the pure oxide, which has been reduced from molybdic acid by the hydrogen of the ammonia. It is of a dark brown colour, but it becomes purple if exposed to solar light; it is nearly insoluble in acids. The hydrated binoxide may be obtained by digesting molybdic acid, mixed with copper filings, in hydrochloric acid; an excess of ammonia precipitates the oxide of a rusty brown colour, whilst the copper is retained in solution. Hydrated binoxide of molybdenum is soluble in pure water, but is precipitated by the addition of any salt. The solution gelatinizes on keeping. The salts which this oxide forms with acids are of a reddish-brown colour, or if anhydrous, are nearly black. If a solution of bichloride of molybdenum be added, drop by drop, to a concentrated solution of bimolybdate of ammonia, a deep blue precipitate of molybdate of molybdenum ( $\text{MoO}_2, 4 \text{ MoO}_3$ ) takes place. This compound is soluble in water, but is precipitated by the addition of any saline body. The addition of a small quantity of a protosalt of tin to a soluble molybdate reduces it, and produces this beautiful blue compound, which may serve as a test of the presence of molybdic acid: care must be taken not to add the tin salt in excess. Another compound of the binoxide of molybdenum with molybdic acid ( $\text{MoO}_2, 2 \text{ MoO}_3$ ) has a green colour.

(692) *Molybdic Acid* ( $\text{MoO}_3$ ), *Eq.* 70, is obtained in an impure state by roasting the sulphide of molybdenum at a low red heat; it remains behind as a dirty yellow powder; caustic ammonia dissolves the acid, leaving oxide of iron and other impurities. The ammoniacal solution crystallizes on evaporation, and by a low red heat the ammonia is expelled, leaving the acid behind, of a pale buff colour. It reddens moistened litmus paper, and is sparingly soluble in water, forming a yellow solution. At a red heat it fuses to a straw-coloured glass of sp. gr. 3.49: it undergoes volatilization in open vessels, and the acid is deposited on cool surfaces in brilliant transparent needles. No definite hydrate of molybdic acid is known. When precipitated from its salts by the addition of an acid, it may be redissolved, if the acid be added in

excess. It is also freely soluble in cream of tartar. Molybdic acid unites with bases, and forms well characterized salts, both neutral and acid. Those of the alkalies are soluble. Neutral *molybdate of ammonia* crystallizes in colourless square prisms. An *acid molybdate of ammonia* ( $2 \text{H}_4\text{NO}$ ,  $5 \text{MoO}_3$ ,  $3 \text{aq}$ ) crystallizes readily in six-sided prisms. Other acid molybdates of the alkalies have been formed, which contain as many as 3, 4, and even 5 equivalents of the acid to 1 of base. Molybdate of lead ( $\text{PbO}$ ,  $\text{MoO}_3$ ) occurs native in crystals of a yellow colour; it is soluble in nitric acid, and in solution of potash if the alkali be in large excess.

Solution of molybdate of ammonia may be advantageously employed in certain cases to detect the presence of very small quantities of phosphoric acid in solution. The solution suspected to contain the phosphate must be acidulated with hydrochloric acid, and the molybdate then added. The liquid becomes yellow, and gradually deposits a yellow crystalline precipitate, consisting of molybdic and phosphoric acids in combination with ammonia. According to Sonnenschein it contains 6.747 per cent. of ammonia.

Sonnenschein takes advantage of the insolubility of this salt to detect small quantities of ammonia by its means. In order to prepare the test solution, he first procures the yellow precipitate, by adding molybdate of ammonia to an acidulated solution of phosphate of soda, ignites the precipitate to expel the ammonia, adds nitric acid to the residue, in order completely to reoxidize any reduced molybdic acid, evaporates to dryness, and expels the nitric acid by ignition. A solution of carbonate of soda is employed to dissolve the remaining mixture of phosphoric and molybdic acids, and the solution is supersaturated with hydrochloric acid. This liquid, it is stated, will easily detect the presence of 1 part of sal ammoniac in 10,000 of water. Salts of soda are not affected by it, but strong solutions of the salts of potash yield a similar yellow precipitate.

(693) Three sulphides of molybdenum are known,  $\text{MoS}_2$ ,  $\text{MoS}_3$ , and  $\text{MoS}_4$ .

*Bisulphide of Molybdenum* ( $\text{MoS}_2$ ), *Eq.* 78; *Sp. Gr.* 4.138.—This sulphide is the principal ore of the metal: it is unchanged by heat in close vessels, but if roasted in the open air, sulphurous acid is formed and is volatilized, while molybdic acid remains. This sulphide may be formed artificially by heating molybdic acid in the vapour of sulphur.

The *Tersulphide* ( $\text{MoS}_3$ , *Eq.* 94), is precipitated by transmitting

sulphuretted hydrogen through a solution of a molybdate, and adding hydrochloric acid. It is of a dark brown colour, and forms sulphur salts with the sulphides of the alkaline metals. The potash salt crystallizes in magnificent iridescent crystals ( $\text{KS, MoS}_3$ ). The *quadrisulphide* of molybdenum also combines readily with the alkaline sulphides.

A *Protochloride of Molybdenum* ( $\text{MoCl, Eq. } 81.5$ ), is obtained by dissolving the protoxide in hydrochloric acid. A *bichloride* ( $\text{MoCl}_2$ ) is procured in deliquescent, fusible, volatile crystals, in appearance resembling those of iodine, by heating the metal in a current of dry chlorine. It is obtained in solution by dissolving the deutoxide in hydrochloric acid.

A *Chloromolybdic Acid* sublimates in yellowish scales when the deutoxide is heated in a current of chlorine. It is soluble both in water and in alcohol, and consists of ( $\text{MoCl}_3, 2 \text{ MoO}_3$ ), or ( $\text{MoO}_2\text{Cl}$ ). Similar compounds may be formed with many acidifiable metals, such, for example, as tungsten, chromium, and vanadium.

#### (694) CHARACTERS OF THE SALTS OF MOLYBDENUM:—

1. Little is known of the *protosalts* of molybdenum. They yield a dark brown precipitate with the *alkalies* and their *carbonates*; the precipitate is soluble in excess of carbonate of ammonia; *sulphuretted hydrogen* slowly produces a brown precipitate of hydrated sulphide which is soluble in hydrosulphate of ammonia.

2. The salts of the *deutoxide* have a dark colour, and a metallic astringent taste. *Infusion of galls* produces a brownish-yellow solution; *ferrocyanide of potassium* gives a dark brown precipitate; *ammonia* a rusty brown precipitate of the deutoxide.

3. The reactions of zinc, tin, and copper, on the *molybdates* are characteristic. With *zinc*, in dilute acid solutions, the liquid becomes first blue, then green, and finally black, after which the addition of ammonia produces a deposit of protoxide of molybdenum. The addition of a small quantity of *protochloride of tin* in solution to a liquid containing a molybdate, produces a beautiful blue molybdate of molybdenum ( $\text{MoO}_2, 4 \text{ MoO}_3$ ), but care must be taken not to have the tin salt in excess, or the precipitate becomes dull green. *Copper filings* in similar solutions reduce the molybdic acid to the deutoxide, which is precipitated as a brown hydrate by ammonia.

Molybdenum is usually estimated in the form of the bisulphide, of which 100 parts contain 58.97 of the metal.

## § V. TUNGSTEN.

*Symbol, W ; Equivalent, 92 ; Specific Gravity, 17.6.*

(695) TUNGSTEN is a metal found in small quantities in the form of an acid combined with lime, in the mineral known as *Scheelite* or tungstate of lime ( $\text{CaO}, \text{WO}_3$ ) : or else in *wolfram* as a tungstate of iron and manganese ( $\text{MnO}, \text{WO}_3$ ) + 3 ( $\text{FeO}, \text{WO}_3$ ). It is easily obtained from the tungstate of lime, by digesting the powdered mineral in hydrochloric acid, which combines with and dissolves the lime, but leaves the insoluble tungstic acid behind : from this compound the metal itself is prepared, by heating it to bright redness in a current of hydrogen gas. It is thus left of a dark grey colour, but it assumes a metallic lustre under the burnisher. If the acid be made into a paste with oil and heated intensely in a crucible lined with charcoal for some hours, tungsten is obtained as a heavy, iron-grey metal, which is very hard, and difficult of fusion. It may be heated in the air whilst in the compact state without sensible change, but in the pulverulent form it burns easily into tungstic acid. Aqua regia and nitric acid convert it into tungstic acid, and the same change is produced by heating it in contact with the alkalis or with nitre.

(696) Two oxides of tungsten are known, viz., a binoxide which does not form salts with acids, and an acid teroxide.

*The Binoxide* ( $\text{WO}_2$ ) is obtained as a brown powder by heating tungstic acid to low redness in a stream of hydrogen; or in copper-coloured scales by adding tungstic acid to dilute hydrochloric acid in which some pieces of zinc have been placed. In the latter form it rapidly attracts oxygen from the air and dissolves in a solution of potash with evolution of hydrogen and formation of tungstate of potash. Wöhler obtains it from wolfram by fusing 1 part of this mineral with 2 parts of carbonate of potash : the melted mass is treated with boiling water, filtered, and mixed with a solution of  $1\frac{1}{3}$  part of chloride of ammonium. The solution is evaporated to dryness and the residue ignited. Upon treating the mass with boiling water, the oxide of tungsten remains as a heavy black powder, which must be washed, first with a weak solution of potash, and afterwards with water. The hydrogen of the ammoniacal salt partially reduces the tungstic acid of the mineral.

With soda the oxide of tungsten forms a remarkable compound of a yellow colour and metallic lustre. It crystallizes in cubes, and is not acted upon by any acid or mixture of acids except

the hydrofluoric; the solutions of the alkalies are equally without effect upon it. If heated in the air it is decomposed and partially converted into tungstate of soda. It is obtained by heating the bitungstate of soda in hydrogen gas: in order to remove the undecomposed tungstate of soda and free tungstic acid, the residue is treated in succession with water, hydrochloric acid, potash, and again with water. Its formula is  $\text{NaO} + 2\text{WO}_2$ .

*Tungstic Acid* ( $\text{WO}_3$ ; *Eq.* 116; *Sp. Gr.* 6.12,) is obtained either by the process already described, from the tungstate of lime, or by heating in a current of air the oxide of tungsten obtained from wolfram by Wöhler's method. Tungstic acid when anhydrous is a beautiful straw-yellow, tasteless, insoluble powder: it is readily soluble in alkaline solutions, from which on the addition of an acid it is thrown down as a hydrate contaminated with the acid employed for its precipitation. The tungstates of the alkalies are soluble. *Tungstate of soda* crystallizes in four-sided tables ( $\text{NaO}, \text{WO}_3, 2 \text{ aq.}$ ). The *bitungstate* may be obtained either anhydrous, or crystallized with 4 equivalents of water ( $\text{NaO}, 2 \text{ WO}_3, 4 \text{ H}_2\text{O}$ ). *Tungstate of ammonia* ( $\text{NH}_4\text{O}, \text{WO}_3$ ) is easily obtained by digesting the acid in excess of ammonia: it crystallizes in needles, from which by ignition in open vessels the ammonia is expelled, and pure tungstic acid remains in the form of the crystals of the salt. A *tungstate of tungsten* ( $\text{WO}_2, \text{WO}_3$ ) of a splendid blue colour, corresponding to the molybdate of molybdenum, may be obtained by a partial reduction of tungstic acid, either by hydrogen gas, or by strongly igniting the tungstate of ammonia in close vessels, or by digesting tungstic acid with zinc and hydrochloric or sulphuric acid.

The most important native ore of tungsten is *wolfram*, which is regarded as a mixture, in variable proportions, of tungstates of the protoxides of iron and manganese. Its specific gravity is very high, being about 7.3. It was this circumstance that gave rise to the name *tung-sten*, the term being a combination of two Swedish words, implying "heavy stone."

Tungstic acid forms several classes of salts, all of which except the neutral tungstates retain a certain number of equivalents of water which are essential to the existence of the salt, and which cannot be replaced by a metallic base. Laurent (*Ann. de Chimie*, **XL**. xxi. 54) enumerates no fewer than six modifications of the acid which require different proportions of base to saturate them. Some of these tungstates when mixed with nitric acid do not at once yield a precipitate of tungstic acid.

(697) Both with sulphur and with chlorine, tungsten forms two compounds, corresponding to the deutoxide of tungsten and

tungstic acid. The *tersulphide* is a strong sulphur acid, and with sulphide of potassium it forms an orange-yellow crystallizable compound.

Both the *chlorides* of this metal are volatile: they are decomposed by water into hydrochloric acid and the corresponding oxide of tungsten.

An *oxychloride* ( $\text{WO}_2 \text{ Cl}$ ) may be obtained in yellow volatile crystalline scales, by passing dry chlorine over the heated binoxide of tungsten. It is sometimes termed *chlorotungstic acid*.

Bichloride of tungsten absorbs ammonia, and by a gentle heat, the whole of the chlorine is expelled in the form of sal ammoniac, leaving a black powder consisting of  $2 \text{ WN} + \text{WH}_2\text{N}$ . When heated in the air it burns, evolving ammonia and leaving a residue of tungstic acid (Wöhler). It is not soluble in acids.

(698) CHARACTERS OF THE SALTS OF TUNGSTEN.—The compounds of this metal are not poisonous. The tungstates in solution are colourless. A *bar of tin*, placed in their solution in a vessel from which air is ~~exhausted~~ <sup>excluded</sup>, produces a deep violet-coloured liquid, owing to the reduction of the acid to a lower degree of oxidation. The addition of any stronger acid to the tungstates causes the separation of a yellow precipitate of tungstic acid contaminated by the precipitant. They yield *before the blowpipe* with borax, a colourless transparent glass, which becomes yellow in the reducing flame, and blood-red on cooling. With microcosmic salt (517) they give a beautiful blue in the reducing flame, which becomes yellow or colourless in the oxidating flame; the addition of a little metallic tin to the bead favours the production of the blue colour.

Tungsten is always estimated in the form of tungstic acid, 100 grains of which contain 79.32 of the metal.

A remarkable similarity exists between the compounds of tungsten and those of molybdenum, and it is worthy of note that the equivalent number of tungsten is exactly double that of molybdenum, whilst its specific gravity is also very nearly double.

## § VI. VANADIUM.

*Symbol, V; Equivalent, 68.46.*

(699) VANADIUM is one of those rare metals at present known only as chemical curiosities; it was discovered in 1830, by Sefström, in a Swedish iron ore from Taberg, but its most abundant ore is the vanadate of lead which has been found at Zinlapan in Mexico, at Wanlockhead in Scotland, and more recently in Chili; lately



Wöhler has found vanadium accompanying some of the ores of uranium and iron. It is best obtained by reducing vanadic acid in a covered porcelain crucible, by means of potassium: the reduction takes place with vivid incandescence; the potash is dissolved by water, and vanadium is deposited as a brilliant metallic powder. By passing a current of dry ammonia over heated chloride of vanadium, the metal is obtained in a coherent form with a steel white lustre; it is brittle and very infusible. It is readily dissolved by nitric acid and aqua regia, forming a fine blue solution; but it is not acted upon even by boiling sulphuric, hydrochloric, or hydrofluoric acids; when heated with the alkalis in close vessels, it undergoes no change.

(700) *Oxides of Vanadium*.—This metal forms three distinct compounds with oxygen,  $\text{VO}$ ,  $\text{VO}_2$ , and  $\text{VO}_3$ . The *protoxide* ( $\text{VO}$ , *Eq.* 76.5) is obtained from vanadic acid by reducing it in a stream of hydrogen, or by charcoal: it is a black crystalline brittle mass, resembling graphite in appearance, and like it conducts electricity. It does not combine either with acids or with bases. If heated in air for some time it absorbs oxygen, forming the *binoxide* ( $\text{VO}_2$ , *Eq.* 84.5) as a black anhydrous powder, which forms salts with acids; they have a blue colour, and when mixed with the alkalis furnish a grey hydrate of the binoxide; in this form it rapidly absorbs oxygen and becomes first brown and then green. Binoxide of vanadium appears also to possess weak acid properties, as it combines with bases.

*Vanadic acid* ( $\text{VO}_3$ , *Eq.* 92.5) is a powerful metallic acid of a brownish-red colour; it is sparingly soluble in water, to which it communicates a yellow tint; the solution reddens litmus strongly. At a red heat it fuses without further change, and crystallizes on cooling, becoming incandescent from evolution of latent heat in the act of solidification. It forms both neutral and acid salts: the neutral salts when first prepared are yellow, but in a few hours they spontaneously become white. The most important of these salts is the *vanadate of ammonia*, ( $\text{NH}_4\text{O}$ ,  $\text{VO}_3$ ), from which the acid itself is usually obtained. Vanadate of ammonia is procured by putting pieces of sal ammoniac into a crude solution of vanadate of potash, such as is prepared by the deflagration of vanadium slag with nitre, after the excess of alkali has been neutralized with hydrochloric acid: the vanadate of ammonia is insoluble in a saturated solution of chloride of ammonium, and is gradually deposited in small crystalline grains. Cold water dissolves it sparingly, but it is much more soluble in hot water: when heated in the open air the ammonia is expelled, and pure vanadic acid is left. The *bivana-*

*diate of ammonia* yields crystals of an orange colour. If mixed with tincture of galls, these salts give a deep black liquid, which preserves its blackness even when much diluted: it forms the best writing ink yet known, as it is not destroyed either by acids, which turn it blue, or by alkalis, or by chlorine.

Vanadic acid appears to combine in different proportions with the inferior oxides of the metal, forming compounds which are either of a green or purple colour. It also combines with many acids in definite proportions, forming compound acids which often crystallize with facility.

The affinity of vanadium for sulphur is but small. It combines with it in two proportions,  $VS_2$ , and  $VS_3$ .

A *Bichloride of Vanadium* ( $VCl_2$ ) may be obtained of a blue colour; and a *terchloride* ( $VCl_3$ ), which is a yellow volatile liquid, is obtained by heating a mixture of vanadic acid and charcoal, in a current of chlorine. Bromides, iodides, fluorides, and cyanides of vanadium have also been formed.

(701) CHARACTERS OF THE COMPOUNDS OF VANADIUM.—1. The *vanadiates* when boiled with either alcohol, or sugar and sulphuric acid, give a beautiful blue solution which distinguishes them from the chromates, which under these circumstances furnish a green liquid. Before the blowpipe with borax, the vanadiates give a green glass, which becomes yellow in the oxidating flame.

2. The salts of the *binoxide of vanadium* give a black colour with tincture of galls, and a grey precipitate with the *alkalies*, becoming red by exposure to the air. *Ferrocyanide of potassium* gives a yellow precipitate which becomes green when exposed to the air. The *alkaline sulphides* give a brownish-black precipitate, readily soluble in excess, and forming a magnificent purple liquid.

## § VII. ANTIMONY.

*Symbol* Sb; *Equivalent* 129. *Specific Gravity*, 6·715.

(702) ANTIMONY is a brilliant bluish-white metal, of a flaky, crystalline texture, and so brittle that it may readily be reduced to powder. It fuses at about  $840^{\circ}$  F., and by slow cooling may be obtained in rhombohedral crystals, which, according to Mitscherlich, are isomorphous with those of arsenic. The commercial cakes of the metal exhibit upon their upper surface a beautiful penniform crystalline structure. At a bright red heat it is volatilized slowly; the operation is facilitated by transmitting a current of hydrogen over it. Antimony is an inferior conductor of heat and

of electricity. When exposed to either a moist or a dry air, at ordinary temperatures, it undergoes no change, but if heated it burns brilliantly, emitting copious white fumes which consist chiefly of teroxide of antimony. It is also oxidized by nitric acid and by boiling sulphuric acid. Aqua regia dissolves it readily. When finely powdered, it is dissolved by strong hydrochloric acid by the aid of heat, with evolution of hydrogen.

This metal is not used alone in the arts, but it enters into the composition of several valuable alloys: *Type metal* is one of these: it is composed of 3 or 4 parts of lead, and 1 of antimony. Music type, in addition, contains tin; and the common white metal used for teapots, under the name of *Britannia metal*, consists of equal parts of brass, antimony, tin, bismuth, and lead. The value of the antimony in these alloys depends upon the hardness which it communicates to the compounds, without rendering them inconveniently brittle, and to the expansion which it confers upon them in the act of solidification, so valuable in the case of type metal. In combination with bitartrate of potash, oxide of antimony forms a powerful and valuable medicine. The teroxide, when ground up with linseed oil, furnishes a pigment which is employed to some extent as a substitute for white lead: it is much less injurious to the health of those who use it than pigments which contain lead.

(703) *Extraction of Antimony*.—Antimony is a tolerably abundant substance, and is always extracted from its sulphide, though it is frequently found alloyed with other metals, and is sometimes met with in the native state.

The sulphide of antimony usually occurs in a matrix of quartz, sulphate of baryta, and limestone. The *crude antimony* of commerce is merely the sulphide freed from the greater part of its earthy impurities. This purification is effected by placing the ore upon the bed of a reverberatory furnace, covered with charcoal powder. The sulphide melts, the earthy impurities float, and the fluid portion is drawn off into an iron basin, and is afterwards cast into loaves or cakes. If it be desired to extract the metal, the sulphide thus purified is reduced to a coarse powder, and again placed upon the bed of a reverberatory furnace: the temperature may be gradually raised to dull redness, but must be moderated to prevent the mass from entering into fusion: in about 12 hours fumes cease to rise, most of the sulphur is expelled, and a red mixture of the oxide and sulphide of antimony remains. During this process copious vapours of sulphurous and arsenious acids are given off, accompanied by a considerable portion of oxide

of antimony. It is stated that nearly 20 per cent. of the metal is lost during this operation. The roasted mass is now mixed with about  $\frac{1}{2}$  of its weight of powdered charcoal, made into a paste with a strong solution of carbonate of soda, and heated in crucibles to bright redness; the metal collects at the bottom; above it is a scoria consisting chiefly of a double sulphide of sodium and antimony. This scoria is known in the arts as the *crocus of antimony*. The metal is remelted with the scoria, and is then fit for sale. 100 parts of sulphide yield about 44 parts of metallic antimony, so that in the whole process about  $\frac{2}{3}$  of the antimony are lost.

On the small scale the metal is most easily procured by taking 4 parts of the powdered sulphide, 3 of crude tartar, and  $1\frac{1}{2}$  of nitre, mixing them intimately, and throwing the powder in small portions at a time into a crucible kept at a bright red heat. The sulphur is oxidized by the nitre, and the metal melts and collects at the bottom.

In order to obtain antimony free from arsenic, Wöhler mixes intimately 4 parts of finely powdered commercial antimony with 5 of nitrate of soda, and 2 of anhydrous carbonate of soda. The mixture is heated to redness in a Hessian crucible, and the antimony burns quietly at the expense of the oxygen of the nitrate. After the deflagration is complete the crucible is covered, and the mass is kept for half an hour at a temperature sufficient to soften but not to fuse it, from time to time pressing it down with an iron spatula. It is removed from the crucible by means of a spatula, whilst still in a pasty condition, then pulverized and thrown into boiling water: the solution contains the arseniate of soda, whilst the greater part of the antimoniate of the alkali remains undissolved, and is well washed with boiling water. From this antimoniate of soda the metal is extracted by melting it with half its weight of tartar.

The product thus obtained is an alloy of antimony with potassium: it is broken into small pieces and thrown into water; a copious disengagement of hydrogen takes place, the potassium is oxidized and dissolved, and the alloy falls to powder. It still retains iron, and, perhaps, lead. One-third of the mass is converted into oxide by means of nitric acid; this oxide is well washed with water, dried, and then incorporated with the powdered metal; the mass is again melted in a covered crucible, and pure antimony is obtained beneath a layer of fused oxide, which retains the oxides of iron and lead.

(704) *Oxides of Antimony*.—Antimony forms three well-marked

oxides; the first is the most important, as it constitutes the basis of the antimonial salts employed in medicine. These oxides are the teroxide (often called the sesquioxide),  $\text{SbO}_3$ , antimonious acid,  $\text{SbO}_5$ , and an intermediate compound of these two, generally termed antimonious acid ( $\text{SbO}_3, \text{SbO}_5$ ).

*Teroxide of Antimony* ( $\text{SbO}_3$ ), *Eq.* 153.—In the anhydrous state this oxide is found crystallized in prisms in a rare mineral called *white antimony ore*, of specific gravity 5.56. The anhydrous oxide is best procured by boiling powdered metallic antimony to dryness in an iron ladle, with excess of strong sulphuric acid; an insoluble sulphate is formed, and sulphurous acid is disengaged. To remove the sulphuric acid, the residue is treated with carbonate of soda and is well washed: the greyish-white insoluble powder which remains is the teroxide. When heated it assumes a yellow colour, but recovers its whiteness on cooling. In close vessels it is fusible; at a high temperature it may be volatilized, and the vapour may be condensed in brilliant crystalline needles isomorphous with the unusual form of arsenious acid. Occasionally it crystallizes in octohedra, like the common variety of arsenious acid. In the open air it burns like tinder, and is converted into antimonious acid. Hydrochloric and tartaric acids dissolve it freely. Nitric acid converts it into one of the higher oxides of antimony. With sulphuric acid it forms an insoluble sulphate. In the hydrated state it may be obtained by pouring a solution of terchloride of antimony into a solution of carbonate of soda. In this form it is readily soluble in solutions of potash and soda; but the simple ebullition or evaporation of the liquid causes a separation of oxide of antimony in prismatic crystals.

(705) *Antimonic Acid* ( $\text{SbO}_5$ ) *Eq.* 169.—This compound may be obtained in the anhydrous form, by oxidizing the tersulphide with nitric acid, and expelling the excess of nitric acid by a heat below redness. Antimonic acid is of a pale yellow colour; it is tasteless and insoluble in water. A strong heat expels one-fifth of its oxygen, and converts it into the antimoniate of antimony ( $\text{SbO}_3, \text{SbO}_5$ ), which is a white powder often termed *antimonious acid*, but which possesses no acid characters, for if treated with bitartrate of potash it is dissolved, tartrate of antimony and potash (*tartr-emetic*), being formed, and separating in crystals, whilst the antimonic acid is retained in solution.

Antimonic acid forms definite compounds with the alkalis: boiling solution of potash dissolves it, and on the addition of an acid, the liquid deposits hydrated antimonic acid in the form of a

white powder ( $\text{SbO}_5, 4\text{H}_2\text{O}$ ), which reddens litmus, and is freely soluble in cold solutions of the alkalies, and in hydrochloric acid. Fremy states that antimonie acid may, like peroxide of tin, be obtained in two modifications, which combine with different amounts of base, and form distinct classes of salts: to one of these modifications he gives the term *antimonie acid*: its neutral salt with potash has the formula ( $\text{KO}, \text{SbO}_5 + 5 \text{aq}$ ): the other modification he terms *metantimonie acid*. To the neutral potash salt of this acid he assigns the formula ( $2\text{KO}, \text{SbO}_5$ ).

According to Fremy, antimonie acid is monobasic, but it is capable of forming both acid and neutral salts. *Neutral antimoniate of potash* may be procured by heating 1 part of metallic antimony with 4 parts of nitre in an earthen crucible. The white mass so obtained is powdered, and washed with warm water, to remove the excess of potash and nitrite of potash. The residue must be boiled with water for an hour or two; the *insoluble anhydrous antimoniate* is thus converted into a *soluble* modification with 5 equivalents of water. The insoluble residue now consists chiefly of biantimoniate of potash. The neutral salt possesses the property of freely dissolving the biantimoniate, which is precipitated when such a solution is mixed with any neutral salt of one of the alkalies. The neutral antimoniate does not crystallize, but forms a gummy mass, which has an alkaline reaction; it is readily decomposed by acids, depositing the biantimoniate. When heated to  $320^\circ$  it loses 2 equivalents of water, and becomes insoluble.

*Biantimoniate of Potash* ( $\text{KO}_2, 2\text{SbO}_5$ ) is obtained by transmitting a current of carbonic acid through a solution of the neutral antimoniate. It is soluble in a hot solution of the neutral antimoniate, and is deposited in crystals as the liquid cools.

If antimonie acid be heated with oxide of lead it combines with it and yields a yellow compound, which is used as a pigment under the name of *Naples yellow*.

(706) *Metantimonie Acid* ( $2 \text{H}_2\text{O}, \text{SbO}_5$ ).—This compound derives its principal interest from the circumstance of its yielding a soluble compound with potash, which may be employed as a test for soda. The *bimetantimoniate of potash* ( $\text{KO}, \text{H}_2\text{O}, \text{SbO}_5 + 6 \text{aq}$ ) is the salt which is used for this purpose. In order to prepare this compound, anhydrous neutral antimoniate of potash is to be first formed by deflagrating antimony with nitre, washing and boiling the residue in the manner already described, so as to bring the whole of the neutral antimoniate into solution. This liquid is then to be filtered and evaporated to a syrupy consistence

in a silver dish; fragments of hydrate of potash are then added, and the evaporation is continued until a drop of the liquid placed upon a cold slip of glass begins to crystallize; it is then allowed to cool, and the alkaline supernatant liquid is poured off the crystals, which are allowed to drain upon a porous tile. When the salt is required as a test for soda, 30 or 40 grains of this residue are to be washed quickly with about twice their weight of cold water and allowed to subside; this washing is to be repeated two or three times, in order to remove traces of adhering potash: lastly, a little water is to be digested for a few minutes upon the residue, and the filtered liquid may be used to ascertain the presence of soda. (Pelouze, and Fremy, *Traité de Chimie Générale*, 2me ed. iii. 156.) The presence of free potash impairs the delicacy of the reaction. One great inconvenience which attends the use of this reagent is the circumstance, that if the solution be kept for a few days, the bimetantimoniate of potash passes spontaneously into the neutral antimoniate, and this salt does not precipitate the compounds of soda; both salts contain exactly the same amount of acid and of base,  $(\text{KO}, \text{HO}, \text{SbO}_5) = (\text{KO}, \text{SbO}_5 + \text{HO})$ , the difference in properties being due, there can be little doubt, to difference in the molecular constitution of the two salts. If the solution of bimetantimoniate be boiled, its conversion into neutral antimoniate is effected in a few minutes. The *bimetantimoniate of soda*  $(\text{NaO}, \text{HO}, \text{SbO}_5, 6 \text{ aq.})$  is an insoluble salt, which crystallizes in octohedra.

(707) *Antimonureted Hydrogen* ( $\text{H}_3\text{Sb}?$ )—The composition of this gas is not known with certainty, as at present it has never been obtained free from hydrogen. It is formed by dissolving an alloy of zinc and antimony in dilute sulphuric acid. When any salt of antimony is poured into a mixture of zinc and sulphuric acid which is disengaging hydrogen, the antimonial salt becomes decomposed; part of the antimony is deposited in the form of a black powder upon the surface of the zinc, and part combines with the hydrogen, and assumes the gaseous state. It forms a colourless gas which is without any marked odour. When burned it deposits white fumes of oxide of antimony, and if transmitted through a glass tube, heated to low redness, the gas is decomposed, and the antimony forms a brilliant metallic crust upon the heated portion of the tube.

(708) *Sulphides of Antimony*.—Two compounds of antimony with sulphur are known; the tersulphide ( $\text{SbS}_3$ ), and the pentasulphide ( $\text{SbS}_5$ ), corresponding to the teroxide, and to antimonio

acid. They are termed sulphur acids by Berzelius, as they combine with the sulphides of the alkaline metals, and form definite salts.

*Tersulphide of Antimony* ( $\text{SbS}_3$ ), *Eq.* 177, *Sp. Gr.* 4.6.—This substance constitutes the only ore from which the metal is obtained. This native sulphide is usually found in granite or slate rocks, and generally contains lead and arsenic, besides a variable amount of pyrites. It occurs crystallized in 4-sided prisms, which have a bluish-black colour, and a strong metallic lustre. It is friable, and melts below a red heat, crystallizing as it cools. It may be distilled unchanged in close vessels, at a very high temperature, but by roasting in the open air it is converted into a fusible mixture of teroxide and tersulphide of antimony. This oxysulphide when fused forms the commercial *glass of antimony*, which contains about 8 parts of the oxide of antimony to 1 of sulphide. If the oxide be in excess, the glass is transparent, and of a fine red colour: the greater the proportion of the sulphide, the darker is the tint. The glass attacks the silica of the crucible in which the fusion is performed, and dissolves a considerable portion of it. A native oxysulphide of antimony occurs crystallized in oblique rhombic prisms ( $\text{SbO}_3 + 2 \text{SbS}_3$ ): it has received the name of *red antimony ore*.

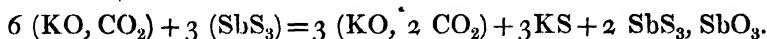
The tersulphide of antimony may be obtained in crystals by melting together, at a red heat, a mixture of sulphur and teroxide of antimony; sulphurous acid escapes, and the tersulphide is formed, thus:  $2 (\text{SbO}_3) + 9\text{S} = 2(\text{SbS}_3) + 3\text{SO}_2$ .

The tersulphide may also be obtained as a hydrate of a beautiful orange colour, by transmitting sulphuretted hydrogen through a solution of any salt of the metal: it parts with its water on being heated, and then assumes a dark metallic appearance, resembling that of the native sulphide. The sulphide, whether artificial or native, is dissolved by hot hydrochloric acid, and furnishes a convenient source of pure sulphuretted hydrogen, provided that the gas be washed, to free it from traces of antimony and hydrochloric acid, which it is apt to retain in suspension.

Tersulphide of antimony is readily soluble in the sulphides of the alkaline metals, and forms colourless compounds; a hot solution of the alkaline sulphide can dissolve much more of the sulphide of antimony than it can retain when cold; on the addition of an acid the alkaline sulphide is decomposed, and the sulphide of antimony is reprecipitated. If sulphide of antimony be boiled with carbonate of potash, or with caustic potash, it is dissolved; the filtered



liquid on cooling deposits a reddish-brown substance, known as *kermes mineral*. This substance is not a definite compound, but is a variable mixture of sulphide and oxide of antimony, the latter being combined with a small portion of the alkali. The action of carbonate of potash on the sulphide is represented in the following equation :—



In this mixture of  $\text{SbS}_3$  and  $\text{SbO}_3$ , H. Rose found crystals of oxide of antimony, which were visible by the aid of the microscope. Bitartrate of potash, or dilute hydrochloric acid, dissolves out the oxide, leaving the sulphide. If to the liquid, after deposition of the kermes, hydrochloric acid be added, effervescence takes place, with escape of sulphuretted hydrogen, owing to the decomposition of sulphide of potassium, and the excess of sulphide of antimony which it retained is precipitated as the *golden sulphide of antimony*. This sulphide contains a larger proportion of sulphur than the tersulphide, from the gradual oxidation of the antimony in the solution before the precipitation is effected.

*Pentasulphide of Antimony*, ( $\text{SbS}_5$ , Eq. 209) or *Sulphantimonic Acid* as this compound is often termed, may be obtained by transmitting a current of sulphuretted hydrogen through an acid solution of perchloride of antimony. It forms an orange-yellow precipitate, which is remarkable for the facility with which it combines with the *alkaline sulphides*. The tribasic *sulphantimoniate of sodium* ( $3 \text{NaS}, \text{SbS}_5 + 18 \text{aq.}$ ), or Schlippe's salt, crystallizes in large and very brilliant transparent tetrahedra. It may be obtained in various ways: the easiest plan consists in thoroughly mixing 18 parts of finely powdered tersulphide of antimony, 12 of dried carbonate of soda, 13 of quick lime, and  $3\frac{1}{2}$  of sulphur; the mixture is ground up with water, and placed in a well-closed bottle, which is completely filled with water; it is allowed to digest, with frequent agitation, for 24 hours; the clear liquid is filtered off, and allowed to evaporate spontaneously in a closed vessel over sulphuric acid. This salt when mixed with an acid deposits pure pentasulphide of antimony.

(709) *Chlorides of Antimony*.—Antimony forms two chlorides,  $\text{SbCl}_3$  and  $\text{SbCl}_5$ ; they correspond in composition with the oxides and sulphides.

*Trichloride of Antimony* ( $\text{SbCl}_3$ ), Eq. 235.5.—This substance, from its ready fusibility, was known under the name of *butter of antimony*; it may be obtained in the anhydrous form by distilling

an intimate mixture of 8 parts of corrosive sublimate with 3 of powdered metallic antimony; it passes over in the form of a volatile, fusible, crystallizable compound, which is deliquescent and powerfully corrosive in its action on animal tissues; calomel terchloride of antimony, and an amalgam of antimony are formed  $2 \text{ Sb} + 4 \text{ HgCl} = \text{SbCl}_3 + \text{Sb}_2\text{Hg}_2 + \text{Hg}_2\text{Cl}$ . Terchloride of antimony may be more cheaply prepared by mixing sulphate of antimony with twice its weight of chloride of sodium, and then distilling the mixture. It may also be obtained by distilling the residue left on dissolving sulphide of antimony in hydrochloric acid. The terchloride of antimony is soluble in hydrochloric acid, and in a small quantity of water; but if thrown into a large mass of water an insoluble oxychloride falls, which gradually assumes a compact crystalline form consisting of  $(2 \text{ SbO}_3 + \text{SbCl}_3)$ ; it was formerly called *powder of uigeroth*. On diluting a hot solution of chloride of antimony in hydrochloric acid with hot water, it deposits, on cooling, brilliant needles which may be represented as  $(\text{SbCl}_3 + 5 \text{ SbO}_3)$ ; by heat, the chloride is sublimed, leaving the oxide. Chloride of antimony is used for bronzing gun-barrels, in order to prevent them from rusting.

*Perchloride of Antimony* ( $\text{SbCl}_5$ , *Eq.* 306.5) is prepared by exposing powdered antimony, gently heated in a retort, to a current of dry chlorine in excess. It forms a volatile, colourless liquid which emits suffocating white fumes when exposed to the air. With a small quantity of water it forms white deliquescent crystals but it is decomposed by a large quantity of water, and antimonious acid, which retains a little hydrochloric acid, is deposited. Dry perchloride of antimony absorbs sulphuretted hydrogen, and forms with it a white crystalline fusible solid ( $\text{SbCl}_3\text{S}_2$ ) which corresponds in composition to the chlorosulphide of phosphorus.

(710) CHARACTERS OF THE COMPOUNDS OF ANTIMONY.—According to M. Peligot (*Ann. de Chimie*, III., xx. 297) teroxide of antimony forms salts which contain 1, 2, or 4 equivalents of acid. Most of them when largely diluted with water become milky from the deposition of a subsalt of sparing solubility, but this milkiness disappears on the addition of tartaric acid, or of bitartrate of potash. They are all of them colourless, and when taken internally in large doses, produce poisonous effects. Infusion of cinchona bark yields a copious insoluble precipitate with antimonial salts, and it has been recommended to exhibit this medicine in cases of poisoning with antimony: it is not however to be relied on.

The characteristic reaction of these salts when in solution is the

formation of an orange-coloured precipitate of hydrated of antimony, when acted on by *sulphuretted hydrogen*; this precipitate is soluble in hydrosulphate of ammonia. For medico-legal purposes this sulphide is separated by filtration, and reduced to the metallic state by heating it in a current of dry hydrogen gas; sulphuretted hydrogen is formed, and the current of gas is continued until no more sulphuretted hydrogen is produced; the tube may then be weighed, and the antimony withdrawn: on again weighing the tube, the difference will give the weight of the metal. Another simpler plan may be adopted, in which antimonuretted hydrogen is first prepared, and subsequently decomposed by heat. In order to effect this, the suspected liquid, after boiling with hydrochloric acid and a little chlorate of potash, is filtered and introduced into Marsh's apparatus; the experiment is then proceeded with in the manner which will be mentioned when speaking of its application in testing for arsenic (719).

(711) *Estimation of Antimony*.—There is considerable difficulty in accurately determining the quantity of this metal. The solution is first acidulated with a mixture of hydrochloric and tartaric acid, then subjected to a current of sulphuretted hydrogen, and exposed for a few hours in an open, shallow dish, at a temperature not exceeding  $100^{\circ}$  F.: the excess of sulphuretted hydrogen is thus got rid of, and the whole of the antimony is separated as sulphide, but the weight of the dried precipitated sulphide of antimony cannot be relied upon as furnishing a correct datum for estimating the metal, as it is liable to contain a variable excess of uncombined sulphur. It must therefore be dried at  $212^{\circ}$ , and a certain proportion of it dissolved in hot aqua regia; as soon as it is completely dissolved, the solution is mixed with a little tartaric acid; and the sulphur, which has by this means been converted into sulphuric acid, is precipitated by the addition of chloride of barium: the sulphur is calculated from the weight of the sulphate of baryta obtained, and deducted from the weight of sulphide of antimony employed; the difference is estimated as antimony. Antimony may be separated by sulphuretted hydrogen from all the metals previously described, with the exception of cadmium, tin, tungsten, and molybdenum. Sulphide of cadmium is not soluble in hydrosulphate of ammonia, whilst that of antimony is soluble; this liquid may therefore be employed to separate these metals.

The separation of antimony from tin in a metallic alloy may be effected with tolerable accuracy by dissolving the alloy in hydrochloric acid, which is to be mixed with a small proportion of nitric

acid, in order to prevent loss of antimony as antimonuretted hydrogen. The two metals are then precipitated together by means of metallic zinc, and the pulverulent metals are weighed. This precipitate is redissolved in weak aqua regia, and is digested at a gentle heat upon a bar of tin, which throws down antimony only. The precipitated metal is collected, washed, dried, and weighed.

### § VIII. ARSENIC.

*Symbol, As; Equivalent, 75; Sp. Gr. from 5.70 to 5.959.*

(712) ARSENIC, in various states of combination, was known to mankind before the Christian era. This element presents many analogies with phosphorus, and it is considered by several French writers to belong to the non-metallic elements. It, however, conducts electricity with facility, and possesses a high metallic lustre.

Arsenic generally occurs, in the form of an alloy with some other metal, especially with iron, or with cobalt, nickel, copper, or tin. It is found occasionally in the native state, and it is sometimes met with united with oxygen combined as arsenic acid with other oxides, constituting arseniates, such as those of iron, copper, and lead. More rarely it occurs united with sulphur, either as the red bisulphide (realgar), or as orpiment, the yellow tersulphide.

The greater part of the arsenic of commerce is prepared from mispickel, an arsenical sulphide of iron, furnished abundantly by the Silesian mines, and from the arsenides of nickel and cobalt, which yield arsenious acid as a secondary product in the ordinary process of working these ores. The separation of the arsenic is effected by roasting the mineral in a manner similar to that employed for driving off sulphur; but the arsenious acid which is produced, being less volatile, more valuable, and more deleterious, is condensed in large chambers, through which the flues from the furnaces pass. The emptying of these chambers, which is performed about once in six weeks, is an operation attended with danger to the workmen, from the poisonous and irritating nature of the finely powdered arsenious acid. In order in some degree to protect the men whilst thus engaged, they are cased in leather, with glazed apertures for the eyes, and are made to cover their mouths and nostrils with damp cloths, which arrest most of the acid particles. Much of the acid obtained from these chambers is in the form of a fine powder; it is still very impure, and it is

therefore again sublimed in iron pots, the upper part of which is kept moderately cool; here it is condensed in a transparent, half-fused, vitreous mass. The lower portions only of this sublimate are pure, and these are sold as white arsenic; the upper are either resublimed, or are employed for the purpose of furnishing metallic arsenic. In order to obtain the metal, the sublimed acid is powdered, mixed with charcoal, and heated in an earthen crucible, upon the top of which a second inverted crucible is luted and screened from the fire by means of a perforated iron plate. The reduced metal is condensed in the upper crucible.

*Properties.*—Metallic arsenic, or *arsenicum*, as it might conveniently be termed, has a brilliant dark steel-grey lustre; it is very brittle, and is easily reduced to powder. When heated to  $356^{\circ} \text{F.}$ , in close vessels, it begins to volatilize without fusing, and crystallizes indistinctly, as it is condensed, in rhombohedra, which are isomorphous with those of antimony. Its vapour is colourless, and possesses a powerful, oppressive, alliaceous odour, and a sp. gr. of 10.60. The metal may be exposed to a dry air without undergoing change. If heated in open vessels it absorbs oxygen, burns with a peculiar bluish flame, and is converted into arsenious acid, which is condensed as a white mealy powder upon cool bodies in the neighbourhood. When thrown in fine powder into chlorine gas it takes fire spontaneously, and is converted into chloride of arsenic. Nitric acid easily oxidizes the metal, and converts it into arsenic acid: if deflagrated with nitre, it is converted into arseniate of potash. A minute quantity of arsenic is added to lead to facilitate its assuming the globular form in the manufacture of shot.

The compounds of arsenic with oxygen are two, arsenious acid ( $\text{AsO}_3$ ), and arsenic acid ( $\text{AsO}_5$ ), no salifiable oxide being known.

(713) *Arsenious Acid* ( $\text{AsO}_3$ , Eq. 79).—This compound is the *white arsenic* of the shops. It is prepared upon the large scale during the roasting of arsenical ores in the manner already described. It exists in two modifications, a vitreous and a crystalline form. When purified by resublimation and freshly obtained, it is in semi-transparent vitreous lamellated masses; but by exposure to the air, it gradually becomes opaque, and of a yellowish-white colour. This change slowly advances from the exterior towards the interior, so that the mass is often opaque at the surface whilst it remains transparent in the centre. Both varieties of arsenious acid are freely soluble in hot hydrochloric acid, and as the liquid cools the excess crystallizes in transparent anhydrous octohedra, consisting of uncombined arsenious acid; but when the

transparent variety is dissolved in this acid, the formation of each crystal is marked by the emission of a flash of light which is perceptible in a darkened room. The opaque variety as it crystallizes from its solution, exhibits no such phenomenon. Hot solution of ammonia also freely dissolves arsenious acid, and deposits it in anhydrous octohedra of the uncombined acid on cooling, mixed with prismatic crystals, which Mr. Bloxam found to be bibasic arsenite of ammonia. Guibourt found the opaque variety to have a specific gravity of 3.699, it is less dense than the transparent form, the specific gravity of which he states to be 3.7385. The two varieties also differ in their solubility: according to M. Bussy, (*Comptes Rendus*, Mai 1847) water dissolves much less of the opaque than of the transparent acid. A cold saturated solution of the vitreous variety gradually deposits its excess of acid in the opaque form, and retains between 2 and 3 per cent. in solution; the liquid reddens litmus. Mere grinding to a fine powder converts the transparent into the opaque variety, and reduces its solubility. Heat, however, gradually reconverts the opaque into the vitreous modification, so that long-continued boiling renders the opaque as soluble as the vitreous form. It is therefore difficult to state the precise degree of solubility of either form of the acid, as the two varieties are liable to be formed in varying proportion in the course of an experiment. The largest proportion which water will dissolve at the boiling point is between 11 and 12 per cent.

Arsenious acid, when heated to  $380^{\circ}$ , softens and is sublimed without fusing, being condensed in transparent octohedra upon warm surfaces, but it occasionally forms long prismatic needles isomorphous with those of oxide of antimony. Its vapour is without odour; it is colourless, and of sp. gr. 13.85; it contains 1 volume of vapour of arsenic and 3 of oxygen, condensed into 1 volume.

Arsenious acid appears to be bibasic; it combines with potash and soda, and forms with them soluble compounds which do not crystallize. The arsenites of the earths (particularly arsenite of lime) are nearly insoluble in water, but are readily dissolved by acids. Arsenite of potash has been used medicinally for many years under the name of *Fowler's solution*. Arsenite of copper is in a commercial point of view the most important of these salts; it is of a delicate and beautiful green colour, constituting the pigment sold under the name of *Scheele's green*. The *Schweinfurth green* which is also used largely as a pigment, is a double salt of arsenite and acetate of copper,  $3(\text{CuO}, \text{AsO}_3) + (\text{CuO}, \text{C}_4\text{H}_3\text{O}_3)$ , made by mixing equal parts of arsenious acid and acetate of copper, in

solution at a boiling temperature, adding an equal bulk of cold water, and allowing the mixture to stand some days.

(714) *Arsenic Acid* ( $\text{AsO}_5$ , *Eq.* 115,) is obtained by treating arsenious acid with nitric acid in excess, and then boiling down to dryness in a platinum vessel. A white, anhydrous, somewhat deliquescent mass remains: from its solution by slow evaporation, arsenic acid may be obtained in hydrated crystals which are very deliquescent. It possesses the properties of a powerful acid, expelling the volatile acids from their combinations, and decomposing the carbonates with effervescence. It forms a series of soluble crystallizable salts with the alkalis, which present considerable interest, as they are isomorphous with the tribasic phosphates. No attempts to procure the dibasic and monobasic forms of arsenic acid have hitherto been successful. Arsenic acid fuses at a high heat, and then becomes decomposed into arsenious acid and oxygen. If a current of sulphurous acid be transmitted through its solution, the arsenic is reduced to the state of arsenious acid, whilst sulphuric acid is formed,  $\text{AsO}_5 + 2 \text{SO}_2 = \text{AsO}_3 + 2 \text{SO}_3$ .

By adding soda in excess to arsenic acid an efflorescent salt ( $3 \text{NaO}$ ,  $\text{AsO}_5$ , 24 aq) may be obtained on evaporation, crystallized in prismatic needles. If to a hot solution of arsenic acid carbonate of soda be added till effervescence ceases, the salt which is obtained on evaporation ( $\text{HO}$ ,  $2 \text{NaO}$ ,  $\text{AsO}_5$ , 24 aq) corresponds in form and composition to the rhombic phosphate of soda, though more usually, it crystallizes with 14 equivalents of water; and by adding to a solution of this compound arsenic acid in excess, a deliquescent salt ( $2 \text{HO}$ ,  $\text{NaO}$ ,  $\text{AsO}_5$ , 2 aq) is procured, which crystallizes with difficulty. The corresponding potash salt crystallizes in bold, brilliant, octohedral crystals ( $2 \text{HO}$ ,  $\text{KO}$ ,  $\text{AsO}_5$ ): it is readily prepared by deflagrating equal parts of arsenious acid and nitre, then dissolving the residue in water, and allowing it to crystallize. All these salts may be rendered anhydrous by heat, but when redissolved, they recover their basic water. A brick-red triarsenate of silver ( $3 \text{AgO}$ ,  $\text{AsO}_5$ ) is precipitated when any of these salts in solution is mixed with solution of nitrate of silver. It is readily soluble in excess either of nitric acid or of ammonia, and is characteristic as a test of arsenic acid.

(715) **SULPHIDES OF ARSENIC.**—Arsenic and sulphur may be melted together in all proportions; but they form several well-defined compounds; of these, the most important are the bisulphide, or realgar,  $\text{AsS}_2$ ; the tersulphide, or orpiment,  $\text{AsS}_3$ ; and the pentasulphide or sulpharsenic acid,  $\text{AsS}_5$ .

*Bisulphide of Arsenic, or Realgar* ( $\text{AsS}_2$ ), *Eq.* 107; *Sp. Gr.* 3.356.

—This substance is occasionally found native in ruby-red prismatic crystals: it may be prepared artificially, by heating together 1 equivalent of arsenic and 2 of sulphur: or, 2 equivalents of arsenious acid with 7 of sulphur; in the latter case 3 equivalents of sulphurous acid are expelled, and 2 equivalents of realgar are formed;  $2 \text{AsO}_3 + 7 \text{S} = 2 \text{AsS}_3 + 3 \text{SO}_2$ . When heated in closed vessels, realgar melts and afterwards is sublimed unchanged. The sublimed mass is hard, brittle, transparent, and of a beautiful red colour. Caustic potash decomposes it, leaving a brown subsulphide of arsenic ( $\text{As}_2\text{S}_3$ ) undissolved. Realgar is one of the ingredients of *white Indian fire*, which is often used as a signal light: it is composed of a mixture of 7 parts of sulphur, 2 of realgar, and 24 of nitre.

*Tersulphide of Arsenic* or *Orpiment* ( $\text{AsS}_3$ , Eq. 123;  $\text{Sp. Gr. } 3.48$ ).—Orpiment is occasionally found native in crystals which have the same form as those of realgar—viz., the oblique rhombic prism: these crystals are flexible; they have a yellow colour and a brilliant lustre. It may be prepared artificially by transmitting a current of sulphuretted hydrogen through a solution of arsenious acid, or of any of the arsenites in hydrochloric acid. It falls as a brilliant yellow amorphous powder. If the solution be very dilute, part of the sulphide is retained in solution, forming a yellow liquid; by exposure to the air the excess of sulphuretted hydrogen escapes, and the sulphide is gradually and completely deposited.

Tersulphide of arsenic is insoluble in water and in dilute acids, but it is decomposed by nitric acid and aqua regia. It fuses easily, and when heated in air burns with a pale blue flame. In close vessels it is sublimed unchanged. Ammonia and the fixed alkalis dissolve it, and form colourless solutions. Hydrosulphate of ammonia and the sulphides of the alkaline metals in solution also dissolve it easily, and form double sulphides which are decomposed on the addition of an acid. Orpiment is the colouring ingredient in the pigment called *King's yellow*, which is a mixture of arsenious acid with this sulphide.

*Pentasulphide of Arsenic* ( $\text{AsS}_5$ , Eq. 155), or *Sulpharsenic acid*, as it is sometimes called, corresponds in composition to arsenic acid. It is prepared by transmitting a stream of sulphuretted hydrogen through a solution of arsenic acid; a yellow precipitate resembling orpiment in appearance, very gradually separates. Upon the application of heat, the pentasulphide fuses and forms a reddish-yellow glassy substance as it cools; it may be sublimed in close vessels. It is soluble in the alkalis, decomposes the carbonates with effervescence if boiled with their solutions, and forms crystal-



lizable compounds with the sulphides of the metals of the alkalies and alkaline earths. The sulphur salt of potash ( $2\text{KS}, \text{AsS}_6$ ) may be made by transmitting sulphuretted hydrogen through the solution of the diarsenate of potash. When this sulphur salt of arsenic is mixed with alcohol, it undergoes decomposition, and a still higher sulphide ( $\text{AsS}_{18}$ ) was obtained by Berzelius; in brilliant yellow crystalline scales, by evaporating the alcoholic solution, after separating the insoluble portion by filtration.

(716) COMPOUNDS OF ARSENIC WITH HYDROGEN.—Arsenic forms two combinations with hydrogen; one of these is solid at ordinary temperatures, and of a chestnut-brown colour. Its composition has not been accurately determined. The other is a gaseous body ( $\text{H}_3\text{As}$ ) of considerable importance; it corresponds in composition to the gaseous phosphuretted hydrogen.

*Terhydride of Arsenic* ( $\text{H}_3\text{As}$ ), *Eq. 78*; *Sp. Gr.* 2.695, *combining Volume*, 4.—*Arseniuretted hydrogen*: this remarkable gaseous compound is an exceedingly poisonous body; it is colourless, and has a fœtid alliaceous odour; it is sparingly soluble in water, and possesses neither acid nor alkaline qualities. It consists of 1 volume of arsenical vapour, and 6 of hydrogen condensed into 4 volumes. By a temperature of  $-40^\circ$  it is reducible to a limpid colourless liquid, which remains liquid at  $-166^\circ \text{F}$ . Arseniuretted hydrogen is inflammable, and burns with a bluish-white flame, which deposits metallic arsenic upon cold bodies introduced within it, and arsenious acid upon those held above it. It is also decomposed when caused to pass through tubes heated to a temperature a little short of redness, metallic arsenic being deposited as a steel-grey crust, whilst hydrogen gas escapes. Chlorine decomposes it with flame, forming hydrochloric acid, and causing the deposition of a solid brown hydride of arsenic. This gas is entirely absorbed by a solution of sulphate of copper, sulphuric acid being liberated, whilst arsenide of copper is precipitated. Nitrate of silver is also decomposed by arseniuretted hydrogen. Solution of corrosive sublimate likewise dissolves it completely, a compound of calomel and arsenide of mercury being formed. It is also largely absorbed by oil of turpentine, with which it forms a crystalline compound.

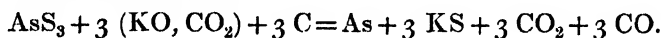
Pure arseniuretted hydrogen may be prepared by decomposing with sulphuric acid diluted with three parts of water, an arsenide of zinc, obtained by heating equal weights of powdered arsenic and granulated zinc in an earthen retort; the fused mass is removed by breaking the retort, and is subsequently powdered. The greatest care is required not to inhale any portion of this deadly

(717) *Terchloride of Arsenic* ( $\text{AsCl}_3$ ), *Eq.* 181.5; *Sp. Gr. of vapour* 6.3.—Only one compound of arsenic with chlorine is known. It is produced either by the combustion of the metal in chlorine, or still better by distilling a mixture of 1 part of arsenicum and 6 of corrosive sublimate; it condenses, as a heavy, colourless, oily looking liquid, which remains liquid at  $-20^\circ \text{F.}$ , and boils at  $270^\circ \text{F.}$ ; it fumes when exposed to the air, and is immediately decomposed by water into arsenious and hydrochloric acids. The *Teriodide of Arsenic* ( $\text{AsI}_3$ , *Eq.* 456), may be prepared by subliming a mixture of 3 parts of iodine and 1 of the metal in a flask; it forms brick-red brilliant flakes. It may also be obtained by digesting 3 parts of powdered arsenic and 10 of iodine in 100 of water; the clear liquid yields red hydrated crystals on evaporation, which become anhydrous when heated to their fusing point: it is soluble in alcohol. A *terbromide* may be formed by analogous means; it is a crystalline solid at all temperatures below  $68^\circ \text{F.}$  The *terfluoride* may be prepared by distilling 5 parts of fluor spar, mixed with 4 of arsenious acid and 10 of concentrated sulphuric acid. It is a fuming colourless liquid, which rapidly corrodes glass, and is decomposed by water.

(718) CHARACTERS OF THE COMPOUNDS OF ARSENIC.—Arsenic forms, with most of the metals, alloys which are generally brittle and easily fusible. The compounds of this metal are all highly poisonous; the substance which has the best claim to be considered as an antidote to it is the freshly precipitated hydrated oxide of iron, which should be suspended in water, and given freely, as early as possible after the exhibition of the poison. It is only applicable when arsenic or arsenious acids have been taken, as it forms an insoluble arseniate of iron; the arsenious acid being partially oxidized by the excess of hydrated peroxide, which is thereby reduced to the form of protoxide of iron. Calcined magnesia may be used if the oxide of iron be not at hand. In cases of arsenical poisoning, putrefaction of the body after death is retarded in a remarkable degree; indeed, in several instances where the body has been disinterred several months after death, it has been found to have been sufficiently preserved from decay to allow many of the principal viscera to be distinguished. In these cases it has not unfrequently happened that yellow patches of sulphide of arsenic have been observed in various parts of the alimentary canal, although it has been ascertained that the poison had been swallowed in the form of arsenious acid. These patches of orpiment are occasioned by the disengagement of sulphuretted hydrogen from the decompo-

sition of the tissues, by which the arsenious acid becomes partially converted into sulphide of the metal.

Arsenic can be identified in quantities so minute as to be inappreciable by the balance. In minerals which contain it, its presence is revealed by the peculiar garlic odour which it emits when a fragment is heated in the reducing flame with carbonate of soda on charcoal *before the blowpipe*. When in solution the compounds of arsenic may be detected by transmitting through the solution, acidulated with acetic acid, a stream of *sulphuretted hydrogen* for six hours; a yellow precipitate is thus produced, which must be further examined as follows: the liquid must be exposed to a temperature of about  $100^{\circ}$  F., in a shallow vessel for six hours, to allow the excess of gas to escape, and the precipitate to subside completely; the clear liquid must be decanted, and the precipitate collected on a small filter. A few drops of ammonia will dissolve it, and on evaporating this solution in a watch-glass by means of a water bath, the sulphide of arsenic will be left. This substance is then subjected to the process of *reduction*, by mixing it with three times its bulk of black flux,\* previously well dried, and introducing it into a glass tube of the diameter of a common quill, care being taken not to soil the sides of the tube. The mixture is gently heated by the small flame of a spirit lamp, and the arsenic is condensed as a brilliant mirror-like ring of steel-grey lustre in the ~~upper~~ part of the tube. The reaction which occurs is explained by the following equation:—



Sulphide of cadmium gives a yellow precipitate with sulphuretted hydrogen, but it is insoluble in ammonia: persalts of tin also give a yellow with sulphuretted hydrogen, but no metallic crust when they are submitted to the process of reduction.

In addition to the preceding tests, arsenious acid may be readily detected in a *neutral* solution by the production of a yellow precipitate with the *ammonia-nitrate of silver*. This reagent is prepared by adding ammonia to a solution of nitrate of silver in very slight excess, so as nearly, but not entirely to redissolve the precipitate of oxide of silver which is at first formed: the clear liquid is decanted for use. The yellow precipitate is an arsenite of silver, which is freely soluble both in ammonia and in nitric acid. As, however, the *tribasic phosphates* give a yellow precipitate with

\* A mixture of carbonate of potash and charcoal obtained by deflagrating equal weights of cream of tartar and nitre in a red-hot earthen crucible.

ammonia-nitrate of silver, and this precipitate also is soluble both in nitric acid and ammonia, a second test should be tried—viz., the *Ammonia-sulphate of copper*, which is prepared from a solution of sulphate of copper, by the addition of ammonia, with the same precautions as those prescribed for the preparation of the silver test. In neutral solutions containing arsenious acid, this copper test occasions a green precipitate consisting of arsenite of copper: it is soluble both in ammonia and in acids. The arsenites of silver and of copper are formed immediately that the tests are added; the sulphide of arsenic does not appear at first if the quantity of arsenious acid be small, as the compounds of arsenic are decomposed by hydrosulphuric acid more slowly than those of any other metal which is precipitable by this reagent.

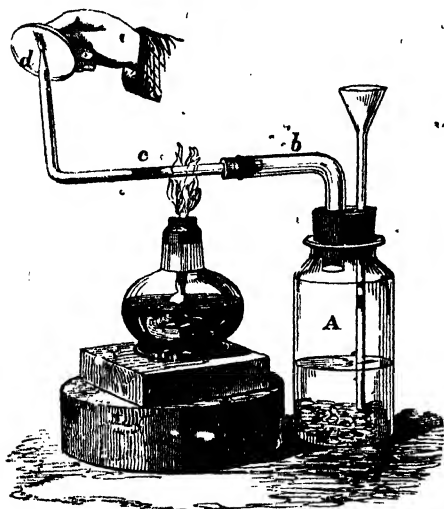
(719) *Search for Arsenic in Organic Mixtures.*—In the greater number of cases, however, where the search for arsenic becomes important, it is mixed with articles of diet, with the contents of the stomach, or with other matters of organic origin, which render preliminary measures needful in order to get rid of them. If the substance be in the liquid form, any sediment which it may contain must be examined for solid particles of undissolved arsenious acid, which are frequently found, and to which the preceding tests are readily applied. If any solid particles of arsenious acid be found, their reduction is easily effected by drawing off a tube to the thickness of a crowquill, sealing one end, dropping in the suspected fragment, adding a minute quantity of dried carbonate of soda, and then a few small fragments of charcoal; upon ignition, the metal is sublimed, and is recognised by the steel-grey ring which it forms in the cool portion of the tube. If no solid particles of the acid be visible, the liquid is boiled and filtered and divided into three portions, one of which is set aside in case of accident.

A second portion is submitted to *Reinsch's test*; it is for this purpose acidulated with hydrochloric acid, and boiled with bright slips of copper foil for half an hour. If any arsenical compound be present, the metal will be reduced upon the surface of the copper foil. The copper is then withdrawn from the liquid, washed, dried at  $212^{\circ}$ , and introduced into a narrow glass tube (about the diameter of a quill), and is then heated nearly to redness; the arsenic combines with oxygen derived from the air in the tube, and is condensed in beautiful transparent octohedra of arsenious acid on the cool part of the tube. The same experiment must be first tried with the copper and hydrochloric acid employed alone, in order to ascertain their purity, before employing them as tests.

The third portion of the liquid is subjected to *Marsh's*

*test*: the application of this test depends upon the formation of arseniuretted hydrogen, and the subsequent deposition of arsenic from it by suitable application of heat.

FIG. 308.



A wide-mouthed bottle, A, fig. 308, of about 6 oz. capacity, is charged with a little pure granulated zinc; through the cork a tube, which of the bottom; a wider tube, *b*, bent to a right angle passes just through the cork, the outer horizontal limb being loosely plugged with asbestos or cotton to arrest any particles of liquid which might be carried up by the effervescence; it is prolonged by fitting into it with a cork, a piece of German tube, *c*, free from lead. Some distilled water is next intro-

duced by the funnel, and a little pure sulphuric acid added to cause a steady evolution of hydrogen. When all the atmospheric air is expelled, the flame of a spirit lamp is placed under the middle of the narrow tube: if after ten minutes, the temperature of the glass being near a red heat, no indications of any metallic deposit show themselves, the materials used are sufficiently pure. Whilst the heat is still maintained, the suspected liquid is to be poured through the funnel into the bottle; if arsenic be present, immediate voltaic decomposition ensues, the arsenic combines with the nascent hydrogen; arseniuretted hydrogen is formed, and the gas is decomposed as it passes through the heated tube; the metal being deposited in the form of a steel-grey ring just beyond the spot where the heat is applied. If the fine tube previous to the experiment had been drawn out to a capillary termination, the gas may be examined as it escapes. It burns with the peculiar flame of arsenic if the quantity be at all considerable, and if a piece of cold white porcelain such as a crucible lid, *d*, be introduced into the burning jet, the more combustible hydrogen is burned, and a brown or grey mirror, like spots of reduced arsenic, may be obtained upon the cold plate. Tartar emetic, if present, would, however, produce antimoniuiretted hydrogen, which, by its decomposition, would give rise to appear-

ances on the tube and on the porcelain resembling those of arsenic. The antimonial spots immediately disappear when a drop of hydrosulphate of ammonia, in which a little sulphur is dissolved, is added, and the solution, by its spontaneous evaporation, leaves the orange hydrated sulphide of antimony; but the arsenical crusts are scarcely acted on by the hydrosulphate (Dr. Guy): a drop of a dilute solution of chloride of lime, on the other hand, immediately removes the arsenical spot, but is without action on that produced by antimony. The chief practical difficulty in the use of Marsh's test, arises from the inconvenient way in which liquids containing organic matter frequently froth up during the operation. The best method of preventing this consists in first boiling the suspected liquid with about a tenth of its bulk of hydrochloric acid, and adding a small quantity of chlorate of potash: the organic matter is thus destroyed, and after the liquid has become cool, it may be safely added to the zinc and sulphuric acid in the apparatus. Marsh's test is one of extraordinary delicacy, and the results are easily and quickly attained. The process by sulphuretted hydrogen and subsequent reduction is also extremely delicate, and open to no objection except the length of time required. Reinsch's test is easy of application, but is not quite so delicate as the other two. The arsenical crusts deposited in the glass tube, are readily sublimed by a gentle heat, and may be converted into arsenious acid, which forms brilliant minute octohedral crystals, and these again may be subjected to the test of the ammonia-nitrate of silver.

Although it may not be possible to detect arsenic in the fluids submitted to examination, it not unfrequently happens that the coats of the stomach, and sometimes the liver, will yet contain the poison in sufficient quantity to render its identification practicable. The best mode of proceeding in this case consists in cutting up the organ into shreds, heating it with an equal weight of hydrochloric acid, the mixture being diluted with water till it becomes of the consistence of a thin paste. Small portions of chlorate of potash are added from time to time until a homogeneous yellow liquid is obtained; when cold it is filtered through linen, the residue well washed, and the clear liquid is concentrated by evaporation (Fresenius and Babo). It is then fit for trial in Marsh's apparatus. Many other tests have been proposed, but they are superfluous, and only tend to introduce an unnecessary complication into the subject.

(720) *Estimation of Arsenic*.—It is not easy to ascertain accurately the quantity of arsenic present in a compound by an analysis; the best plan is one similar to that already directed to be adopted in the case of the quantitative determination of antimony.

The metal should be precipitated in the form of a sulphide; the precipitate should be collected on a weighed filter, dried at  $212^{\circ}$ , and weighed. A given weight of the sulphide is then to be oxidized by means of fuming nitric acid; and when it is completely dissolved, the sulphur is to be precipitated as sulphate of baryta. From the weight of this precipitate the quantity of sulphur is calculated, and deducted from the total amount of sulphide of arsenic; the difference gives the amount of the metal. The sulphide always contains a variable quantity of free sulphur, and hence this method becomes necessary. Before it can be adopted, the absence of all other metals in the sulphide must, of course, be ascertained. By means of sulphuretted hydrogen and the subsequent solution of the sulphide in hydrosulphate of ammonia, arsenic is easily separated from all the foregoing metals, with the exception of those which form soluble compounds with the alkaline sulphides. Its exact separation from tin and antimony is a difficult problem, which has not as yet been solved in a satisfactory manner.

### § IX. TELLURIUM.

*Symbol, Te; Equivalent, 64; Specific Gravity, 6.65.*

(721) TELLURIUM is by most English writers on chemistry classed amongst the metals. It however presents a close analogy with sulphur and selenium, though it possesses a high metallic lustre, and resembles bismuth in colour. It fuses between  $800^{\circ}$  and  $900^{\circ}$  F., and at a high temperature it may be distilled. The latter operation is best conducted by heating the tellurium, very strongly in a porcelain tube, and transmitting a current of dry hydrogen gas over it; the vapour of tellurium is thus mechanically carried forward, and it is condensed in drops and in flexible crystalline needles in the cooler parts of the apparatus. According to Mitscherlich, tellurium when solidified after fusion, possesses a rhombohedral cleavage, a circumstance which appears to indicate its isomorphism with arsenic and antimony. Tellurium is a bad conductor of heat and electricity. When heated strongly in the air it takes fire, burns with a blue flame edged with green, and emits a peculiar characteristic odour, whilst thick white fumes of tellurous acid are produced. Like sulphur and selenium, tellurium is soluble in cold concentrated sulphuric acid, to which it gives a fine purple-red colour; on dilution it is precipitated unchanged.

Tellurium is a rare substance found chiefly in the mines of Hungary, and Transylvania, occasionally native and nearly pure, but generally combined with various metals, such as gold, silver,

bismuth, copper, or lead; it is usually also accompanied by small quantities of arsenic and selenium. Its most common ore is the black foliated tellurium ore of Nagyag, which contains about 13 per cent. of tellurium in the form of tellurides of gold, lead, and silver, mixed with sulphides of antimony and lead. The process of its purification is tedious and difficult; for particulars the reader is referred to the *Lehrbuch* of Berzelius (German Edition, 1844, vol. ii. p. 229). Tellurium forms two oxides, both possessed of feeble acid characters. They correspond in composition to sulphurous and sulphuric acid.

(722) *Tellurous Acid* ( $\text{TeO}_2$ , Eq. 80.)—Tellurium is readily dissolved by nitric acid of specific gravity 1.25. If the solution be poured into water immediately, a white bulky hydrated tellurous acid subsides. It is slightly soluble in water, reddens litmus, and combines with the alkaline bases; these compounds are soluble. Tellurous acid has a bitter metallic taste: it may be obtained in the anhydrous form, by gently heating the hydrate, or by boiling the nitric acid solution, when it is deposited in crystalline needles, which are very slightly soluble in water. The anhydrous acid fuses easily, forming a transparent glass, which is yellow while hot, but becomes white and crystalline on cooling. Tellurous acid possesses considerable volatility: if fused with potash it combines with it. It also combines with the acids like many of the metallic oxides which have acid properties. These salts have a metallic taste, and are said to act powerfully as emetics. Its acid character is very feeble, and its basic property is not more strongly marked: its salts with oxalic and tartaric acid are soluble. All the soluble salts in which this oxide acts as a base are decomposed if mixed with hydrochloric acid, and heated with sulphurous acid: reduced tellurium is precipitated under these circumstances. With sulphuretted hydrogen a black sulphide of tellurium is produced.

*Telluric Acid* ( $\text{TeO}_3$ , Eq. 88) is obtained by gently heating tellurium or tellurous acid with nitre. A tellurate of potash is formed, from which the acid is transferred to baryta, and the baryta is separated by sulphuric acid. It crystallizes in striated hexagonal prisms, which have a nauseous metallic taste; they exert but a feeble action on litmus. These crystals are composed of  $\text{Te}_2\text{O}_3, 3 \text{HO}$ . If heated nearly to redness they become anhydrous, and then assume an orange-yellow colour. In this form telluric acid is completely insoluble in water, or in nitric or hydrochloric acids, or in alkaline solutions. Telluric acid has but a feeble affinity for bases, but it forms salts which contain 1, 2, and 4 equivalents of the acid. When the acid or any of its salts are heated to redness, tellurous acid is formed under disengagement of oxygen.



Two *chlorides*,  $\text{TeCl}$ , and  $\text{TeCl}_2$ , have been obtained; both are volatile; they are decomposed by a large quantity of water.

(723) TELLURETTED HYDROGEN ( $\text{TeH}$ ), *Eq.* 65; *Sp. Gr.* 4.489; *combining Volume* 2.—The most interesting compound of tellurium is that which it forms with hydrogen. It is a gaseous body analogous to sulphuretted hydrogen, and is possessed of weak acid properties. It may be obtained by decomposing the alloy of tellurium with zinc or tin, by means of hydrochloric acid. The gas which escapes reddens litmus, and has an odour which cannot be distinguished from that of sulphuretted hydrogen: with water it forms a colourless solution, which becomes brown by exposure to the air, owing to the oxidation of the hydrogen and separation of tellurium. Telluretted hydrogen precipitates most of the metals from their solutions in the form of tellurides, which have a close analogy with the corresponding sulphides. The alkaline tellurides are soluble in water. Telluretted hydrogen burns with a blue flame.

(724) CHARACTERS OF THE COMPOUNDS OF TELLURIUM.—Tellurium is thrown down from its solutions, in the reduced form by *zinc* or *iron*; neutral solutions of it are also reduced by *protosulphate of iron* or *protochloride of tin*; in these cases the tellurium falls in brown flocculi. The tellurates of the alkalis when heated with charcoal in a test-tube are reduced to tellurides, which are soluble in water and form a red liquid.

## CHAPTER XVI.

### GROUP VI.—BISMUTH, LEAD, COPPER.

#### § I. BISMUTH.

*Symbol*, Bi; *Equivalent*, 212.86; *Specific Gravity*, 9.799.

(725) BISMUTH occurs generally in the native state, and is extracted from its matrix by simple fusion. Its mines occur for the most part in Saxony, Transylvania, and Bohemia. It is not an abundant metal; occasionally it is found as an oxide, or as a sulphide, and sometimes it is combined with tellurium. It generally contains silver, which may be extracted by cupellation. Commercial bismuth is never pure. It is apt to contain a little sulphur and arsenic, which may be got rid of by fusing the metal with about  $\frac{1}{10}$  of its weight of nitre; but it still retains silver, lead, and iron. It may be obtained free from these impurities by solution in nitric acid: the clear liquid is poured into a large bulk of

water. A sparingly soluble subnitrate of bismuth is precipitated. It is washed, dried, and reduced by ignition with  $\frac{1}{10}$  of its weight of charcoal, in a crucible; pure bismuth collects at the bottom.

Bismuth is a hard, brittle metal, of a reddish-white colour; it fuses at  $507^{\circ}$  F., and expands considerably at the moment of congelation: when pure it may be obtained by slow cooling after fusion (69) crystallized in large cubes, which are frequently hollow. Marchand and Scherer found that the density of bismuth was diminished by powerful compression; they thus reduced it from 9.799 to 9.556, probably owing to the formation of minute internal fissures. Bismuth is slightly volatile when strongly heated. It is rapidly oxidized if exposed to the air at a high temperature; boiling sulphuric acid oxidizes it with evolution of sulphurous acid; but its proper solvent is nitric acid, which oxidizes and dissolves it rapidly.

The uses of bismuth are but limited; it is occasionally employed instead of lead in cupellation: some of its compounds are used as pigments, and the subnitrate is employed medicinally. Its most remarkable alloy is that known as *fusible metal*. This is composed of 2 parts of bismuth, 1 of lead, and 1 of tin, or 1 equivalent of bismuth, 1 of lead, and 2 of tin. The mixture fuses a little below  $212^{\circ}$ : passing through a pasty condition previous to complete fusion. According to Erman it dilates in an anomalous manner, when exposed to heat; he states that it expands regularly from  $32^{\circ}$  to  $95^{\circ}$ , then contracts gradually to  $131^{\circ}$ , at which point it occupies a less bulk than it did at  $32^{\circ}$ ; it then expands rapidly till it reaches  $176^{\circ}$ , and from that point till it melts its expansion is uniform. This faculty of expanding as it cools, while still in the soft state, renders the alloy very valuable to the die sinker, as he is able by this means to test the perfection of his die with the greatest accuracy, every line being faithfully reproduced on taking a cast.

Bismuth increases the fusibility of those metals with which it is alloyed, to a very remarkable extent.

(726) *Oxides of Bismuth*.—Bismuth forms two principal oxides, a teroxide ( $\text{BiO}_3$ ), and an acid oxide ( $\text{BiO}_5$ ); besides this there is a compound oxide ( $\text{BiO}_3, \text{BiO}_5$ ), formed by the union of the two preceding combinations.

*Teroxide of Bismuth* ( $\text{BiO}_3$ ), *Eq.* 237, *Sp. Gr.* 8.211.—This compound may be obtained in the anhydrous form, by heating the nitrate or the subnitrate of the metal to low redness. It is a yellow, insoluble powder, which fuses at a red heat, and is easily reduced to a metallic state by heating it with charcoal. A white

hydrate of this oxide may also be procured by precipitating a salt of bismuth by an excess of ammonia.

*Peroxide of Bismuth*, or *bismuthic acid* ( $\text{BiO}_3$ , *Eq.* 253), may be obtained by digesting the washed hydrated teroxide of bismuth in a concentrated solution of potash, and transmitting chlorine gas. A blood-red solution of bismuthate of potash is thus obtained, and a red precipitate is formed, which is to be well washed, and then digested in cold nitric acid to remove the oxide of bismuth with which it is always mixed. A red powder is thus left, which is hydrated bismuthic acid ( $\text{HO}, \text{BiO}_3$ ); by a heat of  $270^\circ$  it is rendered anhydrous, and assumes a brown colour. At a somewhat higher temperature it loses oxygen and becomes converted into the intermediate oxide, or bismuthate of bismuth. According to M. Arppe more than one of these intermediate oxides may be formed. Bismuthic acid combines with the alkalis, but these compounds are decomposed by mere washing with water. The acid is decomposed by concentrated sulphuric acid at ordinary temperatures, and by nitric acid if the temperature be raised.

(727) *Sulphide of Bismuth* ( $\text{BiS}_3$ , *Eq.* 261), occurs native in delicate needles, and in crystals isomorphous with those of tersulphide of antimony. It may be formed artificially by fusing the metal with sulphur: a fusible, dark grey compound, with a feeble metallic lustre, is then obtained; in close vessels it is decomposed into a subsulphide, and into free sulphur, which distils; in the open air sulphurous acid escapes, and teroxide of bismuth remains. When solutions of bismuth are treated with sulphuretted hydrogen, a black precipitate of tersulphide of the metal is formed. Sulphide of bismuth is dissolved by the metal in all proportions, a circumstance which affords an easy method of obtaining it in crystals, as the sulphide crystallizes at a temperature at which the metal still remains fluid.

*Terchloride of Bismuth* ( $\text{BiCl}_3$ , *Eq.* 319), may be obtained by heating bismuth in chlorine, or by mixing the metal in fine powder with corrosive sublimate, and distilling. It is a very fusible, volatile, deliquescent compound; but is decomposed by a large quantity of water into free hydrochloric acid, and an oxychloride of bismuth,  $\text{BiCl}_3, 2 \text{BiO}_3$ , known under the name of *pearl white*.

The *Iodide of Bismuth* is of a dark brown colour, and is insoluble in water, but it forms soluble compounds with hydrochloric acid, and with iodide of potassium.

The only other salt of bismuth of any importance is the *nitrate*, which is easily procured by dissolving the metal in nitric acid. It

crystallizes in large transparent prisms, composed of  $\text{BiO}_3 + 3 \text{NO}_5 + 9 \text{HO}$ , *sp. gr.* 2.376. If the solution be largely diluted with water, a *subnitrate* falls, composed of  $(9 \text{HO}, 4 \text{NO}_5 + 5 \text{BiO}_3)$ , (Becker), called by the old writers *magistery of bismuth*.

(728) CHARACTERS OF THE SALTS OF BISMUTH.—Bismuth presents characters in solution less marked than many metals. Its salts have an acid reaction; and its solutions when diluted become milky from the formation of sparingly soluble subsalts, unless a large excess of acid be present. Iron, zinc, copper, and tin throw down bismuth from its solutions in the metallic state. The *alkalies* give a white precipitate of the hydrated oxide, which is insoluble in excess of the precipitant, and becomes yellow by boiling it with the liquid. Solutions of the *carbonates*, *phosphates*, *tartrates* and *ferrocyanides* give white precipitates with its salts. *Sulphuretted hydrogen* throws down a black sulphide, which is insoluble in hydrosulphate of ammonia. *Chromate of potash* gives a yellow precipitate of chromate of bismuth. *Before the blowpipe* its salts are easily reduced, and yield a brittle bead of bismuth, around which the yellow oxide deposits itself.

(729) *Estimation of Bismuth*.—Bismuth is estimated in the form of the teroxide, 100 parts of which correspond to 89.86 of the metal. Carbonate of ammonia is its best precipitant, but the solution must not contain any chloride or hydrochloric acid, as an oxychloride of bismuth would in that case be precipitated, and part of the bismuth would be volatilized with the chlorine on ignition; the metal must in such a case be precipitated as sulphide. It may be separated from the alkalies, from titanium, and from all the metals of the first four groups, (with the exception of cadmium,) by means of sulphuretted hydrogen; the solution having been first acidulated with acetic acid. From tin, and from the metals of the fifth group, it may be separated by digesting the mixed sulphides (obtained by transmitting sulphuretted hydrogen through the liquid,) in hydrosulphate of ammonia, which leaves the sulphide of bismuth, and dissolves the other sulphides. The sulphide must be dissolved in nitric acid, and precipitated by carbonate of ammonia, which after standing for a few hours throws down the whole of the bismuth in the form of carbonate; it must be ignited in a porcelain crucible; the carbonic acid is thus expelled, and the teroxide of bismuth remains.

Bismuth may be separated from cadmium by the addition of ammonia in excess to the solution of the sulphides in nitric acid; the cadmium is retained in solution, whilst the bismuth is precipitated.

## § II. COPPER.

*Symbol, Cu; Equivalent, 31.75; Specific Gravity, from 8.921 to 8.952.*

(730) The ores of copper are numerous. The metal is frequently found native, crystalized in cubes, octohedra, or dendritic crystals; or else in masses, as in the North American and Siberian mines. In the neighbourhood of Lake Superior there is a vein of massive native copper, associated with silver; this vein is in many parts 2 feet in thickness. The most common ore of copper however is the copper pyrites, or mixed sulphide of copper and iron ( $\text{Cu}_2\text{S}$ ,  $\text{Fe}_2\text{S}_3$ ), which occurs in the primitive rocks, and especially in the *killes*, or clay-slate. More rarely the pure subsulphide of copper ( $\text{Cu}_2\text{S}$ ) is found in the mines of Cornwall and of the Ural Mountains. Other less abundant ores are the blue and green carbonates, and the red and black oxides of copper.

The Cornish mines supply more than two-thirds of the copper which is smelted in Great Britain, but considerable supplies of ore are received from Cuba, Chili, and South Australia. The most important seat of the copper smelting is Swansea, which furnishes annually from 18,000 to 20,000 tons of the refined metal. North America and Saxony supply the larger portion of the remainder. The Australian ore consists chiefly of the green and blue carbonate in a siliceous matrix: these ores contain from 25 to 35 per cent. of copper. Cuba furnishes both the oxides and the sulphides of the metal. Many of the ores from Chili are valuable on account of the large proportion of silver which they contain. The Cornish copper pyrites usually occurs (mixed with small quantities of oxide of tin and arsenical pyrites) in a matrix of quartz, fluor spar, and clay.

(731) The main object in the treatment of such an ore as the Cornish, is to oxidize and remove the sulphur and arsenic in the form of sulphurous and arsenious acids, and to get rid of the quartz and oxide of iron in the form of a fusible slag, composed of silicate of iron combined with other earthy impurities, leaving metallic copper free from admixture.

After the ore has been raised from the mine it is sorted; the purest portions are broken into small pieces of the size of a nut, and the earthy portions are crushed and sifted, as in washing tin ore. The English ore is usually so mixed that it may contain an average of  $8\frac{1}{2}$  per cent. of copper.

The theory of copper smelting as practised at Swansea, like

many other operations, is simple, though the working details appear complicated.\* The principal operations may, however, be enumerated as follows:—

1. Calcining the ore.
2. Melting and granulating for coarse metal.
3. Calcination of the coarse metal.
4. Melting for fine metal.
5. Roasting of the fine metal.
6. Refining and toughening.

We shall make a few remarks upon each of these processes in succession.

(732) 1. *Calcining the Ore.*—The calcination is conducted in large reverberatory furnaces, upon quantities of about 3 tons at a time; the heat is moderate, so as to avoid fusing the mass, which is spread evenly over the floor of the furnace, and stirred at intervals of 2 hours: this roasting is continued for 12 hours, at the end of which time the mass is converted into a black powder containing sulphide of copper, oxide and undecomposed sulphide of iron, and earthy impurities. Oxygen has a stronger affinity for iron than for copper, whilst the affinity of sulphur for copper is greater than for iron; and the effect of the roasting is seen in the production of oxide of iron and sulphurous acid, whilst the sulphide of copper remains unacted upon. During this and the subsequent processes, abundant white deleterious fumes are given off, containing arsenious, sulphurous, sulphuric, and hydrofluoric acids, and a certain portion of metallic arsenic. These fumes hang like a dense canopy over the smelting works and their vicinity; the cloud of *copper smoke*, as it is called, may be discerned at the distance of many miles.

The calcining furnace employed in Wales is shown in section in fig. 309, and a plan of the hearth is exhibited in fig. 310.

*a* is the fireplace; *b*, the bridge; *c c*, the hearth or roasting bed; *d d* are apertures in the floor, through which, by withdrawing an

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\* The apparent complication of the process arises from one of its great practical merits—viz., from the circumstance that it admits of being modified to suit almost every variety of ore, and these modifications necessarily tend to increase its complexity. Le Play enumerates six principal varieties of ores as being wrought by this method.—1. Pyritous ores, containing from 3 to 15 per cent. of copper. 2. Richer ores of the same kind, yielding from 15 to 25 per cent. of copper. 3. Siliceous oxides of copper, yielding from 12 to 20 per cent. 4. Oxides and carbonates with subsulphide of copper, in a siliceous matrix. 5. Very pure siliceous sulphides of copper and iron, yielding from 10 to 15 per cent. of copper; and 6. Pure sulphides and oxides of copper, containing from 60 to 80 per cent. of the metal.

iron slide, the charge can be allowed to pass into the *cub*, or vault *E*, when the roasting is complete; *ff* are the flues; *g* is an opening for the admission of air to the hearth; *н н* are hoppers for charging the furnace, and *t*, a platform over which the barrows of ore are conveyed to the hoppers.

FIG. 309.

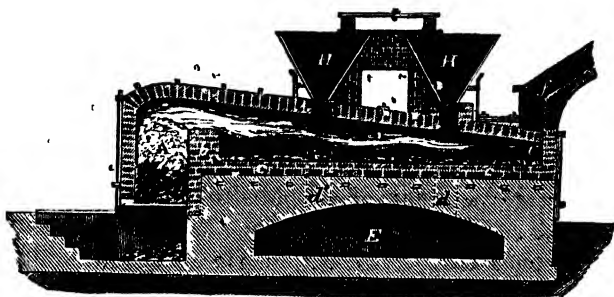
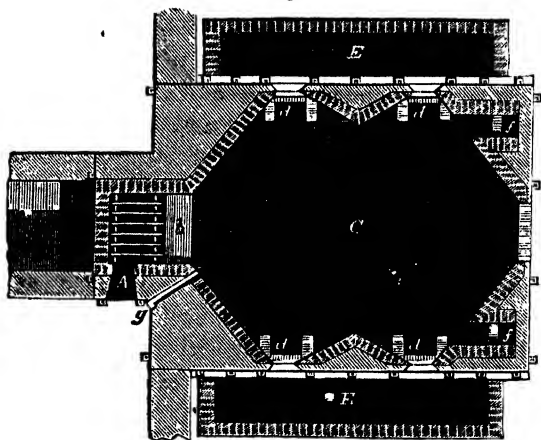


FIG. 310.



The fuel used in roasting the ore is chiefly anthracite, a coal which, under ordinary management, yields no flame. Flame, however, is absolutely necessary to the proper roasting of the copper ore: experience has taught the copper smelter to obtain this desideratum by limiting the supply of air to the fuel in the fire-grate, thus causing the carbonic acid which is formed at the lower part of the fire to be converted into carbonic oxide. By a nice adjustment of the supply of air through *g*, the other apertures of the furnace being closed, the carbonic oxide is gradually burned as it plays over the ore upon the hearth, *c c*; the maximum of heat is thus obtained at the minimum cost of fuel, the carbonic oxide

being completely burned before it reaches the flue. An admirable analysis of this operation is given by M. Le Play in his elaborate memoir on the Welsh method of copper smelting (*Annales des Mines*, IV., xiii. 128).\*

733) 2. *Melting for Coarse Metal*.—The roasted ore is now subjected to fusion with certain proportions of slag, the produce of a subsequent operation, of siliceous ore free from sulphur, and of fluor spar if necessary: by this means the charge is converted into a fusible slag consisting chiefly of silicate of iron, and into sulphides of copper and of iron, which sink through the slag, and form what is termed a *matt*. This fusion occupies about 5 hours, each charge containing about  $1\frac{1}{2}$  ton of roasted ore. The *matt* procured thus contains about 33 per cent. of copper: it is run off while liquid into water, by which it is granulated. The product goes by the name of *coarse metal*. The slag which floats above the *matt* is raked out of the furnace at a separate aperture. It ought to contain no appreciable quantity of metal.

3. *Calcination of the Coarse Metal*.—The granulated metal is again roasted for 24 hours, during which operation a large proportion of the sulphide of iron is converted into oxide.

4. *Melting for Fine Metal*.—A second fusion is performed upon this calcined *matt* with the addition of a portion of copper ore known to be rich in oxide of copper and in silica, and to contain little iron pyrites. By this means the oxide of iron is removed in the form of a fresh slag of silicate of iron, and the oxygen contained in the freshly added oxide of copper completes the oxidation of any portion of sulphide of iron still remaining; the oxide of copper and the whole of the sulphide of this metal being reduced to the state of disulphide of copper ( $\text{Cu}_2\text{S}$ ), or *fine metal*. The slags from this process, and all the subsequent ones, are preserved. This *matt* contains about 80 per cent. of copper. It is cast into pigs. The lower part of these pigs often contain a considerable quantity of tin, and the alloy being the heavier, sinks to the bottom. If a very pure metal be required, the upper parts of the pigs are detached from the lower

\* The heat emitted during the combustion of anthracite is very intense, so that it causes a rapid oxidation of the fire bars of the furnace. This fuel has also the inconvenience of splitting into small fragments, which choke the air ways between the bars, if the heat be suddenly applied. The copper smelter overcomes these difficulties by employing a grate consisting only of a few bars, which do not come into contact with the fuel itself, but only serve as a support for the clinker produced during the combustion of the coal. A bed of clinkers, twelve or sixteen inches thick, rests upon the fire bars, and above this the fuel is burned: from time to time the fireman removes portions of the clinker as it accumulates.—(Le Play.)



portions, and the metal extracted from the upper portions of the ingots is known in the market as *best selected copper*.

5. *Roasting for Blistered Copper*.—The metal is now to be freed from the sulphur, which has hitherto been useful by forming a fusible compound with the copper, thus facilitating its separation from the impurities by which it was accompanied. With this view the pigs of fine metal are next subjected, for several hours, upon the bed of a reverberatory, to a heat just short of that required to fuse them; the metal by this means becomes oxidated at the surface, and a part of the sulphur which it still retains is oxidized; at last it is fused: a remarkable reaction then begins to take place. When oxide of copper and sulphide of copper are heated together, they mutually decompose each other; sulphurous acid and metallic copper are liberated;  $\text{Cu}_2\text{S} + 2 \text{CuO} = \text{SO}_2 + 3 \text{Cu}$ . It is not desirable that the temperature should be too strongly raised, as the oxide of copper would then combine with the silica still present in the mass, and would cease to exert its oxidizing influence. After the charge has become liquid, the temperature of the furnace is therefore allowed to fall; the melted mass solidifies upon its surface, and an appearance of violent ebullition is produced from the formation of sulphurous acid gas, and its efforts to escape from the tenacious mixture: when this ceases, the desulphuration is complete. The temperature is now rendered very intense, the copper melts, and sinks to the bottom, and separates completely from the slag, which consists chiefly of silicate of copper; the reduced metal is then run off into sand moulds. The ingots thus obtained, being full of bubbles, are termed *pimple* or *blistered copper*.

(734) *Refining, or Toughening*.—The blistered copper now undergoes the concluding operation of refining. From 7 to 8 tons of the metal are placed in a reverberatory furnace and kept in a melted state for upwards of 20 hours, in order to oxidate the last traces of foreign metals: during this process a large quantity of oxide of copper is formed; part of this oxide is absorbed by the melted metal, and the copper, if examined at this stage, is found to be of a dull red colour, coarse grained and brittle. To reduce this oxide, the slags are skimmed off, and the surface is covered with a few shovelfull of anthracite or of charcoal, and the metal is subjected to the process of *poling*, in which the trunk of a young tree is thrust into the molten metal. The inflammable gases disengaged from the green wood as it chars, produce a powerful agitation of the whole mass, and in about 20 minutes the poling is finished. The reducing influence of the combustible gases has in the meantime been brought to bear upon every portion of the melted metal. In

this way the oxide diffused through the mass is deprived of oxygen. If the poling be carried too far, the copper again becomes brittle, and is said to be *overpoled*. This defect may be remedied by exposing the surface of the melted metal to a current of air. If too little poling be used, the metal is still brittle, and it is then said to be *underpoled*. There appears to be no doubt that the brittleness of underpoled copper is due to the presence of red oxide of copper in the metal, and Mr. Vivian has suggested that overpoled copper may be defective from the presence of a little carbon. Dr. Percy, however, was unsuccessful in the attempt to discover carbon in overpoled specimens. The progress of the poling, therefore, requires careful watching: the refiner tests the metal from time to time by dipping a small test ladle into the melted mass; a sample of copper is thus removed, and cooled suddenly by immersion in water: the grain of the copper is judged of by cutting the hammered button partially through with a chisel or shears, and then bending it by placing it in a vice. If properly refined, the broken surface will display a fibrous structure with a beautiful satiny lustre. If underpoled, the fracture will be granular, with a number of red points. If overpoled, the fibres become coarser, and the fracture has a strong metallic lustre, but the silky appearance is wanting. When, upon testing, the copper appears to be fine grained, fibrous, and silky, of good colour and malleable, it is either ladled out and cast into ingots, or is cooled suddenly at the surface, by allowing water to run upon it; *rose copper* is thus produced, and successive films are thus made and removed till all the metal is consumed.

The slags from the various operations are carefully remelted, and the copper which is extracted from them is termed *black copper*; it is run into pigs, which are subsequently refined.

The presence of a small quantity of tin in the refined copper is considered advantageous, as the toughness and tenacity of the metal are thereby increased. Antimony is singularly injurious; so small a quantity as 10 ounces in the ton, renders copper unfit for making brass that is required for rolling; and minute traces of nickel are also said greatly to injure the tenacity of the metal.

(735) In the Hartz, and in many mines where the ores contain a large quantity of sulphide of iron, and only about 4 per cent. of copper, the crude mineral is roasted in enormous heaps in the open air. These heaps are in the form of a truncated square pyramid, the base of which is about 30 feet square (340). The roasting is a very slow operation, requiring from 5 to 6 months for its completion. Spring and autumn are the most favourable

seasons in which to commence it. The roasted ore is then subjected to processes not essentially differing from those already described.

In many copper mines the water which is pumped up is impregnated with sulphate of copper derived from the oxidation of the sulphide by exposure to the air: the copper is easily separated in the metallic form, by collecting the water in tanks containing scraps and fragments of iron: the iron unites with the oxygen and the acid, whilst the copper is set at liberty:  $\text{CuO}, \text{SO}_3 + \text{Fe} = \text{FeO}, \text{SO}_3 + \text{Cu}$ .

When the ore consists of the oxides and carbonates of copper, it is easily reduced to the metallic state by simple fusion with coke or charcoal; the copper is rendered tough by a process analogous to that of poling.

The copper of commerce is very nearly pure. It contains minute quantities of arsenic, of iron, of lead, and sometimes of tin and of silver. Copper may be readily obtained in a state of perfect purity, by decomposing a solution of sulphate of copper by means of the voltaic battery: it is then deposited in coherent plates upon the negative electrode.

(736) *Properties*.—Copper is one of the metals which has been longest known to man: before the art of working iron was understood, it was in extensive use, either alone or alloyed with tin, for many of the purposes to which iron is now applied. It is of a well-known red colour, and has a peculiar, disagreeable odour and taste when moistened and rubbed. It is rather a hard metal, very tenacious, ductile, and malleable; after it had been melted beneath a layer of common salt, to exclude atmospheric air, pure copper was found by Scherer and Marchand to have a sp. gr. of 8.921: the density was increased by hammering, and when drawn into fine wire it was obtained as high as 8.952: its fusing point is  $1996^{\circ}\text{F}$ . If exposed to a very intense heat, it is capable of volatilization, but it is usually considered to be fixed in the fire. By slow voltaic action it may be obtained crystallized in cubes and octohedra, and is sometimes found native in these forms. It ranks among the best conductors of heat and electricity. If heated to redness in the open air, copper combines with oxygen rapidly, a layer of oxide is formed upon the surface, and as the oxide contracts more slowly than the metal beneath, it scales off if suddenly cooled, leaving a bright, clean metallic surface. Exposure to a moist air at ordinary temperatures has no effect upon copper; neither has pure water; but in sea water, or in solutions of the chlorides, it is gradually cor-

roded with the formation of an oxychloride of copper. Finely divided copper ignites when touched with a glowing coal, and burns like tinder, being converted into the black oxide. Nitric acid oxidizes and dissolves the metal with rapidity. Oil of vitriol does not act upon it in the cold, but if heated with it, the acid is decomposed, sulphurous acid being evolved and oxide of copper formed, which unites with the excess of acid to form the sulphate. Hydrochloric acid with access of air dissolves it: but if air be excluded, it has no such effect. The fixed alkalies have little action on copper, but ammonia gradually dissolves the metal if the air has access to it, slow oxidation taking place. Before the oxyhydrogen blowpipe it burns with a green flame, and if introduced into a flame of gas or of spirit it communicates to it a green colour. The uses to which copper is applied are very numerous. Vast quantities of it are annually consumed in the sheathing of ships, and in the manufacture of boilers and of various utensils for domestic purposes. It also forms the basis of a number of valuable alloys in extensive use: with zinc it forms the different varieties of brass, and with different proportions of tin, it forms bronze, bell-metal, gun-metal, and speculum-metal (676); whilst its oxides and salts are largely employed as pigments, and furnish articles of some importance in the *materia medica*.

(737) *Brass*.—The combination of zinc with copper has a well-known yellow colour, the tint of which becomes paler in proportion as the quantity of zinc is increased. A curious observation upon this point was made by Mr. D. Forbes, who found that a brittle crystalline alloy of a silver-white colour may be formed, containing 53·49 per cent. of zinc, and consisting of 7 equiv. of copper and 8 equiv. of zinc; or if the quantity of zinc were either increased or diminished, the alloy had the usual yellow colour of brass. The specific gravity of brass is greater than the mean of that of the metals which form it. Brass which contains 25 per cent. of zinc, melts at 1750° F. (Daniell), and a larger proportion of zinc increases its fusibility. By exposure to a long-sustained high temperature in closed vessels, the whole of the zinc may be expelled, and it is not possible to fuse the alloy without losing a portion of the zinc. The alloys of zinc and copper are malleable when cold, but are generally brittle when hot. An alloy prepared by Mr. Muntz, and largely used under the name of *Muntz metal* for the sheathing of ships, may be rolled whilst hot: it contains 2 equivalents of zinc to 3 of copper, or 60 per cent. of copper. Ordinary brass has a sp. gr. of 8·29; it contains about 64 per cent. of copper. The

addition of about 2 per cent. of lead improves its quality if it is to be used at the lathe: it diminishes its toughness, and prevents it from hanging to the tool and clogging the file; but if intended for wire, the presence of lead must be avoided. A very small proportion of tin, even if it does not amount to 1 part in 200, greatly increases the hardness of the alloy. The ordinary solder for brass is an alloy consisting of 2 parts of brass and 1 of zinc. Brass is usually made by melting granulated copper in crucibles, with rather more than half its weight of zinc: formerly a mixture of calamine and charcoal was substituted wholly or partially for metallic zinc. At Swansea, the Muntz metal is prepared by melting the two metals in a reverberatory furnace, which enables a large quantity of the alloy to be prepared with rapidity: but the process is attended with a considerable waste of zinc.

(738) *Oxides of Copper*.—There are two salifiable oxides of copper, both of which are found in the native state; viz., the red oxide or dioxide  $\text{Cu}_2\text{O}$ , and the black oxide  $\text{CuO}$ . Some indications have been obtained of the existence of a still higher oxide, probably  $\text{Cu}_2\text{O}_3$ .

The *Dioxide of Copper* ( $\text{Cu}_2\text{O}$ ; *Eq.* 71·5; *Sp. Gr.* 5·60), occurs native, crystallized either in the octohedron, or in some of its derived forms, or else in capillary crystals or in lamellar masses. There are various ways of obtaining this oxide artificially; one of the best consists in boiling the diacetate of copper with sugar; the oxide of copper contained in the salt is thus deprived of half its oxygen, and the red oxide is deposited in small octohedra. It fuses at a full red heat. By decomposing the dichloride of copper with potash it is obtained as an orange-yellow hydrate  $4 \text{CuO} + \text{aq}$  (Mitscherlich). In this condition it combines with acids. A sulphite as well as a carbonate and an acetate of this oxide appear to exist. The salts of the suboxide of copper are unstable, and absorb oxygen readily. Some of its double salts are more stable: a *double sulphite of copper and potash* may be obtained as a yellow insoluble precipitate, by mixing solutions of sulphite or of bisulphite of potash with sulphate of copper; part of the sulphurous acid being oxidized at the expense of one half of the oxygen of the black oxide of copper.

The anhydrous oxide is resolved by most of the stronger acids into a salt of the black oxide, and into metallic copper. Nitric acid converts it into protoxide and dissolves it: hydrochloric acid converts it into the dichloride. Hydrated dioxide of copper

is soluble in solution of ammonia, forming with it a colourless liquid. This solution is an extremely delicate test of the presence of oxygen in a gaseous mixture; a mere trace of oxygen causes it to assume a blue tint from the formation of the black oxide of copper, which when dissolved in solution of ammonia has an intense blue colour. The principal employment of dioxide of copper is in the manufacture of stained glass, to which it imparts a beautiful ruby or purple colour.

(739) *Black Oxide of Copper* ( $\text{CuO}$ ), *Eq.* 397, *Sp. Gr.* 6.4. —This oxide is a compound of considerable importance to the chemist. It is employed largely as a means of furnishing oxygen to organic substances in the regulated combustion by means of which their composition is determined. The best process for obtaining the black oxide of copper consists in dissolving pure copper in pure nitric acid, and decomposing the resulting nitrate in an earthen crucible, by the application of a red heat. The water and the nitric acid are expelled, and the black oxide remains behind in a state of purity. The heat should be long continued, but not too violent; otherwise the oxide sinters together and concretes into hard masses, which are pulverized with difficulty. A very pure oxide is also furnished by the decomposition of the carbonate by heat; or still more simply by heating a plate of copper to redness in a brisk current of air, and suddenly quenching it in water, in which case the oxide separates in black scales. It may be obtained as a hydrate of a light blue colour ( $\text{CuO}, 2\text{H}_2\text{O}$ ), from any of its salts, by the addition of potash in excess: when boiled with water it becomes black and anhydrous. This hydrate is soluble in ammonia, and gives a splendid blue coloured solution: if slips of metallic copper be introduced into a bottle which is filled with this liquid, and closed so as completely to exclude the air, a portion of the metal, equal to that already in solution, is dissolved, the metal deriving oxygen from the oxide already in solution, both portions being thus reduced to the state of dioxide;  $\text{Cu} + \text{CuO} = \text{Cu}_2\text{O}$ ; the colour gradually disappears, since the dioxide produces a colourless solution with ammonia; but the moment that air is admitted, the blue colour is reproduced. Black oxide of copper is soluble in oils and fats, so that greasy matters boiled in a copper saucepan, which is not kept bright, are liable to become impregnated with the metal. Oxide of copper combines with glass and gives it a beautiful green colour. The oxide is hygroscopic, particularly if in a finely divided state, and it absorbs water rapidly from the air. Its oxygen cannot be expelled from it by mere exposure to heat, but if the oxide be plunged

into an atmosphere of hydrogen while warm, it is decomposed with evolution of light and heat, while water is formed. Black oxide of copper is soluble in most of the acids, and combines with them to form salts which have a green or a blue colour.

Thénard obtained a combination of deutoxide of hydrogen with oxide of copper; it was of a yellowish-brown colour, and when moist quickly underwent decomposition at ordinary temperatures.

(740) *Hydride of Copper* ( $\text{Cu}_2\text{H}$ ).—This substance was obtained by Wurtz, as a brown hydrate, when hypophosphorous acid was mixed with a solution of sulphate of copper, and heated to  $140^\circ$ . It is very unstable: when dry it is suddenly resolved at  $140^\circ \text{F.}$ ; into hydrogen gas and finely divided metallic copper. Hydrochloric acid forms with it chloride of copper, attended with a brisk disengagement of hydrogen. In gaseous chlorine it takes fire spontaneously.

(741) There are two sulphides of copper,  $\text{Cu}_2\text{S}$ , and  $\text{CuS}$ .

• *Disulphide of Copper* ( $\text{Cu}_2\text{S}$ ), *Eq.* 79.5, *Sp. Gr.* 5.0.—This sulphide, which is of a dark grey colour, is occasionally found native in masses, but sometimes in six-sided prisms. It is easily fused by heat in close vessels; nitric acid and aqua regia dissolve it readily. It may be formed by melting together 3 parts of sulphur and 8 of copper; vivid incandescence occurs at the moment of combination. It forms the *fine metal* of the copper smelter.

• The *Sulphide* ( $\text{CuS}$ , *Eq.* 63.7), is obtained in the form of a dark brown hydrate, by decomposing any of the salts of copper by a stream of sulphuretted hydrogen. It is quickly oxidized by exposure to the air, becoming converted into sulphate of copper, and it dissolves easily in nitric acid and in aqua regia.

The *copper pyrites*, or ordinary ore of copper, consists of a double sulphide of copper and iron,  $\text{Cu}_2\text{S}$ ,  $\text{Fe}_2\text{S}_3$ . It is of a yellow colour, and has a brassy lustre: it is found sometimes crystallized in tetrahedra, but it usually occurs in amorphous masses, with a conchoidal granular fracture. It has a specific gravity of 4.3, and is less hard than iron pyrites. The variety, called *variegated* or *peacock ore*, contains a larger proportion of sulphide of copper. These compounds are rapidly oxidized and dissolved by nitric acid or by aqua regia.

• All the sulphides of copper are decomposed by roasting them in air; if the temperature be high, sulphurous acid escapes, and oxide of copper remains behind; at a lower temperature, sulphate of copper is formed.

Sulphide of copper forms likewise a natural combination with sulphides of lead, silver, antimony, and arsenic, constituting grey

copper ore, or *Fahlerz* : this mineral is essentially a quadribasic sulphantimonite and sulpharsenite of copper and iron : it varies considerably in the relative proportions of its constituents, and often contains zinc, lead, silver, and mercury. It crystallizes in forms derived from the regular tetrahedron, and in composition it corresponds to the general formula,  $4 MS, NS_3 + 4 M_2S, NS_3$ , in which M represents the electro-positive metals,  $M_2S$  being usually disulphide of copper or disulphide of silver ; whilst N indicates the electro-negative metals, arsenic or antimony.

The principal varieties of the ore are—

1. *Tennantite*.—A sulpharsenite of copper and iron, of specific gravity 4.375, and of a leaden-grey colour,  $FeS_2.3 CuS, AsS_3 + 4 Cu_2S, AsS_3$ ; the copper in this ore amounts to about 48 per cent.

2. *Light Grey Copper Ore*.—A mixture of sulpharsenite and sulphantimonite of zinc, iron, copper, and silver : specific gravity, 4.5 to 4.7 ; colour, steel-grey.

3. *Dark Grey Copper Ore* contains little or no arsenic. It is of an iron black colour ; specific gravity, 4.7 to 4.9. This variety, and the one preceding it, contain from 35 to 40 per cent. of copper.

4. *Silver Fahlerz* is a dark grey copper ore, rich in silver ; specific gravity about 5.0. The silver varies in this ore from 13 to 30 per cent., and the copper from 14 to 25 per cent.

A native *selenide of copper* is found in combination with selenide of silver. It occurs in masses of a leaden grey colour, and is very rare, having, hitherto, been found only in Sweden : selenide of copper may be formed artificially by precipitating the sulphate of copper by seleniuretted hydrogen.

(742) Copper forms two chlorides,  $Cu_2Cl$ , and  $CuCl$ .

The *Dichloride* ( $Cu_2Cl$ , *Eq.* 99, *Sp. Gr.* 3.376,) is obtained by dissolving 4 parts of finely divided copper and 5 of the black oxide in hydrochloric acid ; or by boiling the chloride with sugar ; or by digesting the chloride in close vessels with metallic copper : the last is a slow process, but part of the dichloride is then deposited in transparent tetrahedra. Dichloride of copper is a white compound, which is insoluble in water, but soluble to some extent in hydrochloric acid, with which it forms a pale brown solution : it fuses easily into a yellowish mass. Dichloride of copper is soluble in a boiling solution of chloride of potassium ; and if the liquid be allowed to cool excluded from the air, octohedral crystals, composed of ( $2 KCl, Cu_2Cl$ ), are deposited. When the solution in muriatic acid is exposed to the air, a pale bluish-green insoluble oxychloride of copper ( $CuCl, 3 CuO, 4 aq$ ) is deposited. This oxychloride is used in the arts as a pigment, under the name of *Brunswick green*. It



is best procured by exposing copper clippings to the action of hydrochloric acid, or to a solution of sal-ammoniac in the open air. It occurs native in the form of a green sand, composed of small rhombic prisms, which is found at Atacama in Peru; it has hence been called *Atacamite*. Sometimes it is also found massive. Other oxychlorides of copper of less importance may also be formed.

(743) The *Chloride* ( $\text{CuCl}$ , *Eq.* 67·2, *Sp. Gr.* 3·054,) may be obtained by the spontaneous combustion of copper in chlorine, but it is more advantageously prepared by dissolving the oxide or the carbonate in hydrochloric acid. A concentrated solution of chloride of copper is of a green colour, but it becomes blue on dilution, and when the salt is anhydrous it is liver-coloured. When heated it fuses, and at a red heat half its chlorine is expelled, and the dichloride remains; the chloride is deliquescent, and very soluble in alcohol. It crystallizes from its aqueous solution in green needles with 2 equivalents of water, of specific gravity 2·534.

A *double chloride of copper and ammonium* ( $\text{H}_4\text{NCl}, \text{CuCl}$ , 2 aq) is obtained by mixing hot concentrated solutions of the two salts in the proportion of one equivalent of each. Anhydrous chloride of copper rapidly absorbs ammonia and forms a blue powder ( $\text{CuCl}$ , 3  $\text{H}_3\text{N}$ ; Rose), which by a heat of  $300^\circ$  loses 2 equivalents of ammonia, and becomes green ( $\text{CuCl}$ ,  $\text{H}_3\text{N}$ ; Kane). Graham and Kane regard this latter compound as chloride of ammonium, in which the fourth equivalent of hydrogen has its place occupied by copper; hence Graham terms it *chloride of cuprammonium* ( $\text{CuH}_3\text{N}, \text{Cl}$ ).

If ammoniacal gas be transmitted through a concentrated solution of chloride of copper, till the precipitate at first formed is redissolved, the liquid on cooling deposits small dark blue, square prisms, and octohedra, ( $\text{CuCl}$ , 2  $\text{H}_3\text{N}$ , aq).

(744) The *Diiiodide* of copper ( $\text{Cu}_2\text{I}$ , aq), is a white insoluble powder, which becomes yellow when heated. It is formed by pouring a mixture of 1 equivalent of protosulphate of iron and 1 of sulphate of copper into a solution of any iodide,  $2(\text{CuO}, \text{SO}_3) + 2(\text{FeO}, \text{SO}_3) + \text{KI} = \text{KO}, \text{SO}_3 + \text{Fe}_2\text{O}_3, 3 \text{SO}_3 + \text{Cu}_2\text{I}$ . Sulphite of soda may be substituted for the sulphate of iron in this experiment. It has been proposed to employ such a mixture of the two sulphates of iron and copper as a test for determining the quantity of iodine in kelp, in order to fix its commercial value.

The *dibromide* of copper is also insoluble in water.

(745) *Sulphate of Copper, Blue Vitriol* ( $\text{CuO}, \text{SO}_3 + 5 \text{ aq}$ ), *Eq.* 79·7 + 45, *Sp. Gr. anhydrous* 3·631, *crystallized* 2·19.—This salt is manufactured on a large scale, by boiling copper in an iron pot

with sulphuric acid, in a concentrated form: the acid is decomposed and the copper is oxidized at its expense whilst the salt is precipitated. It may also be formed from an artificial sulphide of copper, by roasting it with free access of air, and lixiviating the roasted mass to dissolve the sulphate thus formed: the heat must be moderate, or else the sulphate would be decomposed during the roasting. If copper pyrites be used instead of the artificial sulphide, the salt will contain a large quantity of sulphate of iron, which cannot be separated by crystallization. The only plan in such a case is feebly to ignite the mixed sulphates: the iron parts with its acid at a lower temperature than the copper, and by a second solution the iron is separated in the form of an insoluble oxide. Sulphate of copper is also obtained in considerable quantity as a secondary product in the refining of silver: the silver is precipitated from its sulphate in the metallic form by plates of copper, and a pure sulphate of copper is thus furnished.

Large quantities of the sulphate of copper are used in calico printing, and it is the salt from which most of the pigments of copper are formed. It is soluble in 4 times its weight of water at  $60^{\circ}$ , and crystallizes in beautiful blue crystals of an oblique rhombic form. When rendered anhydrous by heat, it assumes the appearance of a white powder, which becomes blue on the addition of water: it is insoluble in alcohol. When heated to bright redness the acid is expelled, and black oxide of copper is left.

If a solution of 1 equivalent of sulphate of copper is boiled with less than 1 equivalent of hydrated oxide of copper, a green insoluble *trisulphate* ( $3 \text{ CuO}, \text{SO}_3, 2 \text{ aq}$ ) is formed. *Brochantite* is a native subsulphate of the metal, composed of ( $4 \text{ CuO}, \text{SO}_3 + 4 \text{ aq}$ ); and Mr. D. Smith obtained a subsulphate consisting of ( $5 \text{ CuO}, \text{SO}_3 + 6 \text{ aq}$ ). Sulphate of copper forms double sulphates both with potash and with ammonia; they are easily obtained by mixing solutions of the salts in equivalent proportions, and allowing them to crystallize. The potash salt is composed of ( $\text{CuO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6 \text{ aq}$ ), sp. gr. 2.244; the ammonia salt of ( $\text{CuO}, \text{SO}_3 + \text{H}_4\text{NO}, \text{SO}_3 + 6 \text{ aq}$ ), sp. gr. 1.891. According to Graham, a hot saturated solution of double sulphate of copper and potash deposits a double salt, the composition of which is represented by the remarkable formula  $\text{KO}, \text{SO}_3 + 3 (\text{CuO}, \text{SO}_3) + \text{CuO}, 4 \text{ H}_2\text{O}$ .

Anhydrous sulphate of copper absorbs dry ammoniacal gas; the compound consists of  $2 (\text{CuO}, \text{SO}_3) + 5 \text{ H}_3\text{N}$  (H. Rose). If ammonia be added in excess to a solution of sulphate of copper, the liquid on evaporation yields dark blue crystals,  $\text{CuO}, \text{SO}_3$ ,

$2 \text{H}_3\text{N} + \text{HO}$  (Berzelius); the salt, when heated to  $300^\circ \text{F}$ ., becomes green, losing one equivalent of ammonia and one of water.

(746) *Nitrate of Copper* ( $\text{CuO}, \text{NO}_5, 6 \text{ aq}$ ), is easily made by dissolving copper in nitric acid: it forms a beautiful blue efflorescent salt, which crystallizes in rhomboidal prisms. Above a temperature of  $60^\circ \text{F}$ . it crystallizes in deliquescent needles of sp. gr. 2.047; they contain 3 equivalents of water. It is very soluble in alcohol; by heat it is decomposed, first into a green *subnitrate* ( $\text{CuO}, \text{NO}_{5.4}, 3 (\text{CuO}, \text{HO})$ , (Gerhardt), sp. gr. 2.765), which is insoluble; and if the heat be increased, it is converted wholly into the black oxide of copper, the whole of the acid being expelled.

Several basic *phosphates* of copper are found native in small quantities.

(747) *Carbonates of Copper*.—All attempts to procure the neutral carbonate of copper have hitherto failed. A *hydrated oxycarbonate*, called *Chessylite* ( $\text{CuO}, \text{HO} + 2 (\text{CuO}, \text{CO}_2)$ , sp. gr. 3.8), forms a beautiful blue mineral, which crystallizes in oblique rhombic prisms. But the most abundant of the carbonates of copper is the hydrated dicarbonate or *malachite* ( $\text{CuO}, \text{HO} + \text{CuO}, \text{CO}_2$ ; sp. gr. 3.7 to 4.0). It forms a very hard mineral of a silky lustre, and a beautiful green colour; it is susceptible of a high polish, by which its concentric and often beautifully veined structure is advantageously displayed. It is often employed for ornamental purposes. Malachite is occasionally found in oblique prisms. Both the blue and the green carbonate are abundant in the copper ore furnished from Australia. A green precipitate, sometimes used as a pigment, which has the same composition as malachite, may be obtained by mixing hot solutions of sulphate or nitrate of copper and carbonate of soda. If the solutions be mixed cold, a pale blue voluminous precipitate is formed; which, according to Brunner, is the same compound, with an additional equivalent of water ( $\text{CuO}, \text{HO} + \text{CuO}, \text{CO}_2 + \text{HO}$ ). By boiling the precipitated carbonate, it becomes first green and then black, losing nearly all its water and carbonic acid. A double carbonate of potash and copper ( $\text{KO}, \text{CO}_2 + 5 \text{ CuO}, 4 \text{ CO}_2 + 10 \text{ aq}$ ) may be obtained by digesting the green carbonate in a solution of bicarbonate of potash: it is deposited in blue crystals by spontaneous evaporation. Similar salts may also be formed with soda and ammonia.

(748) *CHARACTERS OF THE SALTS OF COPPER*.—Most of the salts of copper have a green or a blue colour; they are almost all soluble. They have a strong, disagreeable, metallic taste, and act as poisons

to the animal frame, producing violent and irrepressible vomiting and purging, followed by exhaustion and death. They form an insoluble compound with albumen, which is nearly inert; raw whites of eggs should therefore be administered in cases of poisoning suspected to be occasioned by this metal. Milk or sugar mixed with iron filings, by reducing the salts of copper to salts of the dioxide, or to the metallic state, are also valuable adjuncts.

The salts of copper are easily recognised when in solution. *Potash and soda* give a pale blue voluminous precipitate of hydrated subsalt; an excess of the alkali does not dissolve it, but converts it into a blue hydrated oxide, which becomes black and anhydrous when the liquid is boiled with it. If sugar or tartaric acid, or certain other organic substances be present, the blue precipitate is redissolved by an excess of the alkaline liquid, and forms a blue solution. *Ammonia* gives a similar blue precipitate, but an excess of the alkali redissolves it, forming a deep blue solution, which is very characteristic. *The carbonates of potash and soda* give a pale blue hydrated carbonate, which becomes black when boiled in the liquid. *Carbonate of ammonia*, also, gives a blue precipitate, but redissolves it if added in excess, forming an intensely blue solution. *Ferrocyanide of potassium* yields a bulky brown precipitate. *Sulphuretted hydrogen* gives even in acid solutions a brownish-black hydrated sulphide. The two last characters distinguish the salts of copper from those of nickel, which also form a blue solution with ammonia. Sulphide of copper is insoluble in ammonia, or in hydrosulphate of ammonia. Another characteristic and very delicate test of the presence of copper is afforded by the action of a polished plate of *iron*, which, in a feebly acid solution, is speedily covered with a red deposit of metallic copper. *Zinc* precipitates copper in the form of a black powder, which assumes a metallic lustre under the burnisher. If heated with soda on charcoal before the blowpipe in the reducing flame, a metallic bead of copper may be obtained from the salts of the metal, which may be recognised by its colour and its malleability.

In cases where the presence of copper is suspected in admixture with organic matters, as in the contents of the stomach, where it is supposed to have acted as a poison, the material must be reduced to dryness, and incinerated in an earthen crucible. The ash is then to be treated with nitric acid, and the liquid is tested with ammonia, with ferrocyanide of potassium, and with a slip of polished iron.

The salts of copper have considerable tendency to form double

compounds with other salts, and frequently subsalts of this metal may be procured with various acids: those with the sulphuric nitric, carbonic, and acetic acids, are the most important.

(749) *Estimation of Copper*.—This is generally effected in the form of the black oxide, 100 parts of which correspond to 79·82 of the metal. If the solution contain no metal precipitable by potash, an excess of potash is added, and the liquid is boiled; the precipitate is well washed with boiling water.

Pelouze (*Ann. de Chimie*, III. xvi. 426) has described a method of estimating the quantity of copper, by bringing it into solution with excess of ammonia, and ascertaining the quantity of a standard solution of sulphide of sodium which is required to decolorize the liquid. The process is rapid, and admits of being applied in a large number of cases.

Copper may be readily separated from the metals of the first four groups, with the exception of cadmium, by the action of sulphuretted hydrogen. The precipitated sulphide of copper must be washed with water containing sulphuretted hydrogen in solution, in order to prevent its oxidation on the filter. The precipitate must be detached from the filter, redissolved in nitric acid (610), and the oxide of copper precipitated by means of potash.

If cadmium be present, Stromeyer directs that the precipitate of the mixed sulphides, obtained by transmitting sulphuretted hydrogen through the liquid, be redissolved by nitric acid, and precipitated by an excess of carbonate of ammonia, which, if left to stand for a few hours, dissolves the copper, but leaves the cadmium in the form of carbonate.

The metals of the fifth group are separated by precipitating them with the copper as sulphides, and then digesting the mixed sulphides with a solution of sulphide of potassium (sulphide of ammonium dissolves traces of copper); the sulphide of copper alone remains undissolved.

The separation of copper from bismuth may be effected by means of carbonate of ammonia, as directed for cadmium.

### § III. LEAD.

*Symbol*, Pb; *Equivalent*, 103·57; *Specific Gravity*, 11·44.

(750) Almost all the lead of commerce is obtained from galena, or the sulphide of lead. It occurs, mixed with quartz, blende, pyrites, sulphate of baryta, and fluorspar, in veins traversing the

primitive rocks, and particularly in the clay slate in Cornwall, and mountain limestone in Cumberland. England and Spain furnish the principal supply of this metal. Small quantities of carbonate and phosphate of lead are frequently met with, but they are unimportant as ores of the metal. Galena always contains a small proportion of sulphide of silver; when the mineral is found in bold well-characterized cubes, it is usually nearly pure. The proportion of silver in galena is liable to considerable variation; a mineral yielding 120 ounces of silver to the ton, or 0.36 per cent., is considered extremely rich.

(751) *Extraction.*—After the lead ore has been raised to the surface, it undergoes a careful mechanical preparation, conducted upon the principles already explained (436), and having been thus freed to a great extent from its earthy impurities, it is ready for smelting.

If the galena be tolerably free from siliceous gangue, this operation is sufficiently simple. About  $1\frac{1}{2}$  ton of the dressed ore is mixed with from  $\frac{1}{4}$  to  $\frac{1}{2}$  of its weight of lime, and is heated to dull redness in a reverberatory furnace, through which a strong current of air is passing. A large quantity of the sulphur burns off as sulphurous acid, and a portion of oxide of lead is formed; another portion of the sulphide of lead is converted into sulphate of lead, and much of the ore still remains undecomposed. During the operation, the mass is frequently stirred, and care is taken not to allow the temperature to rise sufficiently high to fuse it. When the roasting is thought to have been carried far enough, the materials in the bed of the furnace are thoroughly mixed together, the furnace doors are closed, and the heat is suddenly raised. The oxide and the sulphate of lead then react upon the undecomposed sulphide of the metal; a large quantity of sulphurous acid is evolved, whilst metallic lead runs copiously from the mass. The successive stages of this operation may be traced as follows:—

One equivalent of sulphide of lead, by combining with 3 equivalents of oxygen, furnishes 1 equivalent of oxide of lead and 1 of sulphurous acid, as is exhibited by the equation:  $\text{PbS} + 3\text{O} = \text{PbO} + \text{SO}_2$ . If the equivalent of galena unite with 4 equivalents of oxygen, 1 equivalent of sulphate of lead is formed:  $\text{PbS} + 4\text{O} = \text{PbO}, \text{SO}_3$ . Both of these compounds, when heated with fresh sulphide of lead, are decomposed, metallic lead and sulphurous acid being in each case the result of the reaction. Two equivalents of oxide of lead and 1 of galena furnish 3 of lead and 1 of sul-

phurous acid :  $2 \text{ PbO} + \text{PbS} = 3 \text{ Pb} + \text{SO}_2$ . One equivalent of sulphate of lead, when heated with 1 of galena, yields 2 equivalents of lead and 2 of sulphurous acid : thus  $\text{PbS} + \text{PbO}, \text{SO}_3 = 2 \text{ Pb} + 2 \text{ SO}_2$ . During the roasting a portion of subsulphide of lead,  $\text{Pb}_2\text{S}$ , is also produced. This substance forms a fusible matt, which flows from the furnace with the metallic lead, constituting a stratum which floats above the melted metal. This subsulphide of lead is again returned to the furnace and roasted with fresh ore.

After the melted mass has been drawn off into cast-iron basins placed for its reception, a few spadefuls of lime are thrown in to solidify the scoræ which remain behind in considerable quantity : these scoræ usually contain an excess of oxide and sulphate of lead : they are therefore mixed with coke or charcoal, and exposed to the cat on the bed of the furnace, after the doors have been carefully closed ; the lime combines with the acid, and the oxide of lead is reduced by the carbon.

*Refining of Lead.*—Lead which contains antimony or tin is subjected to a further operation, termed *improving*, in order to refine it. This consists simply in melting the lead, and heating it for a period, longer or shorter, as may be necessary, in a shallow cast-iron pan set in the bed of a reverberatory furnace ; the antimony and tin being more oxidizable than the lead, are thus removed in the pellicle of oxide which is continually forming. From time to time the workman takes out a small sample of the metal to examine the appearance which it presents on cooling. As soon as it exhibits a peculiar flaky crystalline appearance on the surface, the oxidation has been carried far enough, and the metal is then run off and cast into pigs.

(752) *Concentration of Silver in Lead by Pattinson's process.*—Silver may be profitably extracted from lead, even when the quantity does not exceed from three to four ounces of silver to the ton, by a process introduced by Mr. Pattinson, of Newcastle. This gentleman observed that if melted argentiferous lead be briskly stirred during slow cooling, a portion of the metal solidifies first, in the form of crystalline grains, which sink to the bottom of the portion which remains melted. These crystals consist of lead nearly free from silver ; the fusing point of the argentiferous alloy occurring at a lower temperature than that of pure lead. This observation is turned to account in the following simple manner :—

•Eight or nine cast-iron pots, each capable of containing about five tons of melted lead, are arranged in a row, set in brickwork, and each provided with a separate fireplace underneath. A quantity of lead is introduced into the middle pot, and melted ; the

fire is then withdrawn, and the metal is briskly stirred by the workman whilst it cools: the crystals of lead subside as they form, and are removed at intervals by means of a large perforated iron ladle, and transferred to the next pot on the right hand. When about  $\frac{1}{4}$ ths of the metal is thus removed in grains, the concentrated argentiferous alloy is ladled out into the next pot on the left hand side, and the empty pot is charged with a fresh portion of lead, which is subjected to a similar treatment. When the pot to the right and to the left has in this manner received a sufficient quantity either of poor or of argentiferous lead, it is subjected to a similar operation; the concentrated argentiferous portion being passed off continually to the next pot on the left, whilst the crystalline or poorer portion is handed over to the next pot on the right hand side. The last pot to the left thus at length becomes filled with lead which may contain 300 ounces of silver to the ton; it is not found advantageous to concentrate it beyond this point: the lead which accumulates in the last pot on the right hand side does not contain more than half an ounce of silver in the ton. This poor lead is much improved in quality by the operations which it has undergone, and is at once cast into pigs for the market.

(753) *Extraction of Silver from Lead by Cupellation.*—The rich argentiferous lead is now subjected to *cupellation*. This process is founded upon the circumstance that lead, if exposed at a high temperature to a current of air, rapidly absorbs oxygen, and is converted into a fusible oxide, whilst silver does not become oxidized, but is left behind in the metallic state. The litharge or oxide of lead melts at a high temperature, and flows off the convex surface of the melted metal, and thus continually exposes a fresh surface of lead to the action of the air.

In England the cupellation is performed in a reverberatory furnace, the hearth of which is moveable. This hearth or *cupel* consists of an oval shallow basin composed of a mixture of bone ash with a little wood ashes; this mixture is slightly moistened, and beaten into an iron ring about 4 feet in its long diameter, and 2 feet in the shorter: the cupel is introduced into the furnace from beneath, and is supported by bricks, so that it can be readily removed and renewed,—an operation which is generally required once a week. When dry, the fire is cautiously lighted, and the lead introduced; a continual blast of air from a tuyère is made to play over the surface of the melted metal; litharge is formed abundantly, and runs off through a gutter for the purpose, into an iron pot placed beneath the furnace for its reception. Fresh lead is



added from time to time to supply the place of that which is oxidized ; until at length a quantity of lead, originally amounting to about 5 tons, is reduced to between 2 and 3 cwt. This melted metal is withdrawn by making a hole through the bottom of the cupel ; the aperture is afterwards closed with fresh bone ash, and another charge is proceeded with. When a quantity of rich lead sufficient to yield from 3000 to 5000 ounces of silver, has thus been obtained, it is again placed in a cupel, and the last portions of lead are removed. It is found advantageous to effect this final purification on the concentrated silver lead separately, because in the last stages of the operation the litharge carries a good deal of silver down with it : these portions of litharge, therefore, on being reduced, are again subjected to the desilvering process.

The litharge from the first fusion is either sold as oxide of lead, or it is reduced in a small reverberatory furnace with anthracite, or powdered coal. The porous cupels absorb a large quantity of litharge, and they likewise are passed through the furnace in order to extract the metal.

A very beautiful phenomenon, known as the *fulguration* of the metal, attends the removal of the last portions of lead from the silver. During the earlier stages of the process the film of oxide of lead, which forms constantly over the surface of the melted mass, is renewed as rapidly as it is removed ; but when the lead has all been oxidized, the film of litharge upon the silver becomes thinner and thinner as it flows off ; it then exhibits a succession of the beautiful iridescent tints of Newton's rings ; and at length the film of oxide suddenly disappears, and reveals the brilliant surface of the metallic silver beneath.

In the Hartz the hearth of the cupellation furnace is fixed, and is made of brick, covered with marl, which is renewed after each operation, but the cover of the furnace is moveable.

(754) In the North of England, the galena is smelted by a process somewhat different : the ore is first roasted, and then reduced in a small square blast furnace, or forge hearth, dried peat being the fuel principally employed. This form of furnace is known as the *Scotch furnace*.

In some parts of the Hartz, where the ores are largely mixed with siliceous matters, the English method of smelting is not applicable, as the silica combines with oxide of the lead, and forms a fusible slag. It is found necessary in these cases to reduce the sulphide of lead by means of metallic iron, which is added in the form of granulated cast-iron, in the proportion of about 1 part of

iron to 20 of pure galena. The fusion is performed in a small blast furnace, about 20 feet high, and 3 feet across at the widest part.

In these various furnace operations white fumes are continually disengaged, which consist principally of oxide and sulphur of lead, and are technically termed *froth of lead*; and in this way nearly  $\frac{1}{4}$  of the whole lead is volatilized. Independent of the waste thus occasioned, the fumes are highly deleterious; it is therefore of great importance to prevent their diffusion through the air as far as possible. It is stated, that in the Hartz about  $\frac{1}{10}$  of the volatilized portion is arrested by causing the gases from the furnaces to pass through a succession of condensing chambers, before they finally escape into the air. About 55,000 tons of lead are annually raised in England, which furnish, on an average, 150,000 oz. of silver.

(755) *Properties.*—Lead is a bluish-white metal, so soft that it may easily be made to take impressions; it leaves a streak upon paper, and may be cut with the nail. It may be laminated into tolerably thin sheets, as well as drawn into wire; but both in ductility and tenacity it is low in the scale. It fuses at  $620^{\circ}$  (Person), and may with some difficulty be obtained in cubic or in octohedral crystals as it cools. Lead contracts considerably at the moment of its solidification, and it is therefore not well adapted for castings. It appears to have the power when melted of dissolving a small quantity of oxide of lead, by which the hardness of the metal is much increased (Pelouze and Fremy); but its softness may be restored by keeping it melted under charcoal for some time, with occasional agitation. It is an inferior conductor of heat and electricity.

(756) *Combined Action of Air and Water on Lead.*—The surface of a piece of lead when freshly cut presents a high metallic lustre, but it soon tarnishes by exposure to air, owing to the formation of a thin, closely adhering film of oxide, which protects the metal from further change. Lead undergoes no alteration in a perfectly dry atmosphere, and even when sealed up in a vessel of pure water, which has been boiled for some time to expel the air, the metal will retain its brilliancy for an indefinite period, but if it be exposed to the united action of air and pure water, it is subject to a powerful corrosion. As the result of this exposure, the lead becomes oxidated at the surface, the water dissolves the oxide of lead; this solution absorbs carbonic acid, a film of hydrated oxy-carbonate of lead ( $\text{PbO}, \text{H}_2\text{O} + \text{PbO}, \text{CO}_2$ ) is deposited

in silky scales, and a fresh portion of oxide is formed and dissolved by the water; thus a rapid corrosion of the metal takes place. This action is modified very materially by the presence of various salts in the water, even though the quantity of these salts may not exceed 3 or 4 grains in the gallon. The corrosion is much increased by the chlorides and nitrates, but it is diminished by the sulphates, the phosphates, and the carbonates. Oxide of lead, indeed, is scarcely soluble in water which contains these salts in solution. Bicarbonate of lime is especially remarkable for the preservative influence which it exerts, and as this latter is a very usual impurity in water, few spring waters act on the metal to any dangerous extent. In these cases a film of insoluble carbonate of lead is formed upon the surface, and the metal beneath is protected from further injury. The action of water on lead is a matter of great importance in its sanitary bearings, on account of the extensive employment of this metal in cisterns and pipes for the storage and supply of water. Rain water as collected from the roofs of houses, is for the most part sufficiently impure, especially in large towns, to prevent its action upon the metal. Of all the salts of lead the hydrated oxycarbonate is the least soluble, pure water not taking up more than 1 part in 4 millions, or about  $\frac{1}{4000000}$  of a grain per gallon. If a solution of oxide of lead in distilled water, containing 4 or 5 grains to the gallon, be exposed to the air, it soon becomes filled with silky crystals of the hydrated oxycarbonate, owing to the absorption of carbonic acid; and in a few hours the water does not contain more than  $\frac{1}{4000000}$  of the metal in solution. Water highly charged with carbonic acid may nevertheless dissolve lead to a dangerous extent, owing to the solubility of carbonate of lead in excess of carbonic acid; when water thus impregnated with lead is boiled, the gas is expelled, and the carbonate subsides. So general, however, is the action of water upon lead, that it is rare to find any that has been kept in cisterns of this metal perfectly free from all traces of it. Slate cisterns are therefore greatly to be preferred to leaden ones.

At high temperatures, lead absorbs oxygen rapidly from the air; it undergoes partial volatilization, and emits white fumes of oxide. It is not acted upon by sulphuric or hydrochloric acid at ordinary temperatures, and but slightly even when boiled with them; but it is dissolved with extrication of binoxide of nitrogen by nitric acid, especially when the acid is somewhat diluted. The alkalis do not exercise any decided influence upon it. In the presence of moisture, lead is corroded when in contact with sul-

phate of lime ; hence in its application to architectural purposes, the contact of stucco or plaster with lead should be avoided.

The lead of commerce is often nearly pure. The purest specimens are the softest. Traces of tin, iron, copper, and silver, and sometimes of antimony and manganese, are the impurities which are most often observed. In order to obtain it perfectly pure, it should be reduced with black flux from the oxide left by igniting the pure nitrate of the metal.

(757) From its softness, fusibility, durability, and the ease with which it may be worked, lead is applied to a multiplicity of uses. The reception chambers in the manufacture of sulphuric acid are lined with it. It forms the ordinary material for cisterns, water-pipes, and gutters, and is frequently employed in covering the roofs of houses. In combination it is also very largely employed. The red oxide enters in large proportion into the constitution of flint glass. The carbonates, the oxychlorides, and the chromates are extensively used as pigments, and its alloys are numerous and important. Shot for fowling-pieces is an alloy of lead, with a small proportion of arsenic, which hardens it and facilitates its granulation into globules ; the quantity of arsenic varies with the purity and softness of the lead ; usually it requires from 3 to 8 parts in 1000. The common white arsenic of the shops is added to the lead, melted in a covered vessel, the arsenious acid is reduced by the lead, and the oxide of lead thus formed rises as a film to the surface of the alloy.

When alloyed with about one-fourth its weight of antimony, lead forms type metal. This alloy is sufficiently fusible to allow of its being readily cast ; it expands at the moment of solidification, and copies the mould accurately ; it is hard enough to bear the action of the press, and yet not so hard as to cut the paper. The ordinary *fusible metal* contains lead, as do the various compounds called pewter, Britannia metal, and Queen's metal. The solder used by tinplate workers and plumbers is a mixture of lead and tin (676).

(758) *Compounds of Lead with Oxygen*.—Lead forms 4 oxides ; —an unimportant black dioxide,  $Pb_2O$  ; a protoxide,  $PbO$ , which is the basis of the ordinary salts of the metal ; a binoxide,  $PbO_2$ , which is insoluble in acids ; and red lead, which is a compound of the two oxides last mentioned, usually in the proportions indicated by the formula ( $2 PbO, PbO_2$ ).

*Protoxide of Lead* ( $PbO$ ), *Eq.* 111·57 ; *Sp. Gr.* 9·2 to 9·5.—This oxide is well known under the name of *litharge* : it is the

only salifiable oxide of lead. Its colour varies according to the mode of its preparation. Usually it is obtained on a large scale by the oxidation of lead in a current of air, in which case it forms a scaly mass, which, if of a yellow colour, is commonly termed litharge of silver; if redder, it is termed litharge of gold. The former is the purer, as the red colour is due in many cases to the presence of a small quantity of minium. If the oxidation be effected at a temperature below that required for the fusion of the oxide, a yellow powder termed *massicot* is obtained. Common litharge, when reduced to a fine powder, also has a dull yellow colour; when heated, it assumes a brown-red colour, which disappears again as it cools. Protoxide of lead may be obtained of a beautiful rose colour, by saturating a hot solution of caustic soda, of sp. gr. 1.42, with the oxide, as the liquid cools, anhydrous rose-coloured crystals are deposited. If the solution of oxide of lead in caustic soda be allowed to evaporate spontaneously by exposure to the air, the alkali gradually absorbs carbonic acid, and the oxide is deposited in transparent anhydrous dodecahedral crystals.

If a salt of lead be precipitated by the addition of a caustic alkali, in slight excess, the oxide of lead is precipitated in the form of a white hydrate ( $2 \text{ PbO}, \text{H}_2\text{O}$ ). Another hydrate ( $3 \text{ PbO}, \text{H}_2\text{O}$ ) may be obtained in groups of transparent octohedrons, or of 4-sided prisms mixed with anhydrous crystals, by precipitating solution of triacetate of lead by an excess of ammonia, at a temperature of  $86^\circ \text{ F}$ .

Both litharge and the hydrated oxide of lead absorb carbonic acid readily from the atmosphere.

Protoxide of lead fuses at a heat above redness, and crystallizes on cooling in semi-transparent scales. When fused, it combines rapidly with the earths and with silica, speedily destroying and penetrating the crucibles in which it is melted. The oxide is slightly soluble in water, to which it communicates an alkaline reaction. The presence of a very small quantity of saline matter diminishes or prevents the solution of the oxide; the solution rapidly absorbs carbonic acid from the air, and mere filtration in many cases causes the deposition of a large portion of the oxide in the form of hydrated oxycarbonate.

Oxide of lead is soluble in solutions of the caustic alkalies, and forms compounds with the alkalies and alkaline earths, which have been obtained in crystals; they are, however, decomposed by simple exposure to the atmosphere, owing to the absorption of carbonic acid. The solution of the oxide in lime water is sometimes

used as a hair dye: the lime softens and partially decomposes the hair, and the lead of the oxide combining with the sulphur of the hair, forms sulphide of lead, which stains the hair of a permanent black.

Oxide of lead is a powerful base. It has a strong tendency to form subsalts; those which it yields with acetic acid, and some of those with nitric acid are soluble; they exert a strong alkaline reaction upon test paper, and absorb carbonic acid with avidity. Indeed, owing to the very sparing solubility of the basic carbonate of lead, a solution of a subsalt of lead is the most delicate test for the presence of carbonic acid, either in a gas or in distilled water; a mere trace of carbonic acid occasions the formation of the peculiar silky crystalline precipitate which characterizes the basic hydrated carbonate of lead.

(759) *Minium or Red Lead* is a compound of protoxide of lead with the peroxide of the metal. Its most usual composition is represented by the formula,  $2 \text{PbO}, \text{PbO}_2$ , but it was obtained by Berzelius as  $\text{PbO}, \text{PbO}_2$ , and well crystallized samples have been formed, which consisted of  $3 \text{PbO}, \text{PbO}_2$ . All these compounds possess a brilliant red colour.

Red lead is obtained by heating metallic lead, so as first to procure the protoxide or massicot, keeping the temperature below the fusing point of the oxide; the oxide so obtained is finely levigated in water, and the particles which are held in suspension are allowed to subside, dried, and exposed in iron trays, to a heat of about  $600^\circ \text{F}$ ., in a reverberatory furnace. The additional quantity of oxygen is gradually absorbed. The principal use of red lead is in the manufacture of flint glass. Much care, however, is required in the preparation of minium for this purpose. It is necessary that it should be free from the oxides of other metals, which would impart colour to the glass. In the oxidation of the lead, which constitutes the first stage in the preparation of red lead, the metals which are more oxidizable than lead are removed with the first portions of oxide: whilst the copper and silver accumulate in the portions of oxide which are produced last. The intermediate stage of the operation is therefore that which furnishes the purest oxide. Minium is better suited to the glass maker than litharge, as the excess of oxygen burns off any combustible matter which may accidentally be present, and converts the protoxide of iron into peroxide. Other less important applications of red lead are to the colouring of red sealing wax, and to paper staining.

If minium be exposed to a high temperature it is decomposed, oxygen is evolved, and the protoxide of lead remains. Minium is insoluble in the acids, but by many of them, especially by nitric acid, it is decomposed; a salt of the protoxide is formed, and the brown peroxide of lead remains behind.

(760) *Peroxide of Lead* ( $\text{PbO}_2$ ), *Eq.* 119'57.—This compound is insoluble in water and in acids; it is converted by heat under disengagement of oxygen into the protoxide; sulphurous acid instantly decomposes it, forming sulphate of the protoxide;  $\text{PbO}_2 + \text{SO}_2 = \text{PbO}, \text{SO}_3$ . If digested in ammonia, mutual decomposition occurs, water, nitrate of ammonia, and protoxide of lead are formed. With hydrochloric acid a chloride of lead is produced, and chlorine is set free. If mixed with  $\frac{1}{5}$  of its weight of sulphur, the mixture takes fire by friction; sulphurous acid and sulphide of lead being produced.

Peroxide of lead appears to possess the properties of a feeble acid. By fusing the pure peroxide with excess of caustic potash or of soda, in a silver crucible, and dissolving the residue in a small quantity of hot water, crystals of *plumbate* of potash or of soda are formed as the solution cools: plumbate of potash consists of  $\text{KO}, \text{PbO}_2$ , 3 aq (Fremy). Pure water decomposes these compounds, and the peroxide of lead subsides. Like the peroxides of silver and of manganese, the peroxide of lead is a conductor of electricity, and is formed at the zincode of the battery when aqueous solutions of the protosalts of lead are decomposed by the voltaic current. Peroxide of lead is usually prepared by levigating minium very finely, and digesting the powder in boiling nitric acid, diluted with 4 or 5 times its bulk of water; the residue is washed with fresh nitric acid, and then with water, till everything soluble is removed. It may also be obtained by gently heating a mixture of 4 parts of litharge in fine powder, with 1 of nitrate of potash, and washing the product with water.

(761) *Compounds of Sulphur with Lead*.—The most important of these is the protosulphide,  $\text{PbS}$ , the *galena* of mineralogists. Besides this, a subsulphide,  $\text{Pb}_2\text{S}$ , is formed as the *lead matt* in reducing galena, and a red persulphide is also obtainable, though its composition is not accurately known. This persulphide is procured by adding a solution of an alkaline persulphide to a solution of a salt of lead.

•• *Protosulphide, or Galena* ( $\text{PbS}$ ); *Eq.* 119'57; *Sp. Gr.* 7'59.—Galena is an abundant mineral, and forms the principal ore of lead; it is a brittle substance, and is found crystallized, more or less distinctly, in cubes of a deep leaden colour and strong metallic

lustre. It may be formed artificially either by fusing lead with sulphur or by precipitating any of its salts by sulphuretted hydrogen. When heated in close vessels, part of the sulphur is expelled, and a subsulphide ( $\text{Pb}_2\text{S}$ ) left; this subsulphide is formed on the large scale in the process for reducing galena; it is, however, decomposed by a moderate heat, as the lead melts out in the metallic form, leaving the protosulphide, which, though fusible, is less so than the metal itself. Galena, when heated in contact with air, is oxidated, part of the sulphur burns off, and a mixture of oxide of lead and sulphate of lead is formed. Nitric acid and aqua regia decompose it, converting it into sulphate: hydrochloric acid acts but slowly upon it. When fused with lime or the alkalis, metallic lead is obtained. If heated with oxide of lead or of iron, it is reduced with escape of sulphurous acid.

(762) *Chloride of Lead* ( $\text{PbCl}$ , *Eq.* 139.) is best prepared by precipitating a solution of nitrate of lead by the addition of solution of chloride of sodium; a sparingly soluble, white, heavy precipitate occurs. It is soluble in about 33 parts of boiling water, but it is taken up more sparingly if an excess of hydrochloric acid be present. It is easily fusible into a semi-transparent, horny, sectile mass, and at high temperatures may be volatilized; the alkalis at first convert it into an oxychloride, and if the action be prolonged, into pure oxide.

The chloride combines with oxide of lead in several proportions. One of these forms a white fusible colourless mineral ( $\text{PbCl}$ , 2  $\text{PbO}$ ), which is found in the Mendip Hills. Mr. Pattinson manufactures a white oxychloride of lead by acting on powdered galena with hydrochloric acid. The chloride of lead thus obtained is dissolved in hot water and precipitated, by the addition of lime water, in quantity just sufficient to remove half the chlorine;  $\text{CaO} + 2 \text{PbCl} = \text{CaCl} + \text{PbO}$ ,  $\text{PbCl}$ . This oxychloride ( $\text{PbO}$ ,  $\text{PbCl}$ ), has been used to some extent as a pigment instead of white lead. Another oxychloride ( $\text{PbCl}$ , 7  $\text{PbO}$ ) is a pigment of some importance, known under the name of *patent yellow*, or *Turner's yellow*; it forms a very fusible compound of a bright yellow colour, which may be obtained by heating together 1 part of sal ammoniac and 10 of litharge.

When an acid solution of chloride of lead is precipitated by a current of sulphuretted hydrogen, the precipitate which is first formed is of a bright red colour, but by the further action of the gas it becomes black, and furnishes sulphide of lead: the red compound is a *chlorosulphide* of lead (3  $\text{PbS}$ , 2  $\text{PbCl}$ ).

(763) *Iodide of Lead* ( $\text{PbI}$ ), *Eq.* 230.5, is easily obtained by



precipitating the nitrate or acetate of lead by iodide of potassium; it is thrown down as a bright yellow powder, sparingly soluble in cold water, but more soluble in hot water; the solution deposits beautiful yellow spangles of silky lustre on cooling.

The iodide of lead forms double salts with the iodides of the alkaline metals. Several oxyiodides of lead may also be formed.

A remarkable compound of oxyiodide of lead with carbonate of lead ( $\text{PbI}$ ,  $\text{PbOI}$ ) + 4( $\text{PbO}$ ,  $\text{CO}_2$ ), of a blue colour, may be obtained by precipitating the tribasic acetate of lead with a mixture of 1 equivalent of biiodide of potassium and 4 equivalents of carbonate of potash. Fluoride of lead is white and insoluble.

(764) *Sulphate of Lead*, ( $\text{PbO}$ ,  $\text{SO}_3$ ), *Eq.* 151.57; *Sp. Gr.* 6.30. —This compound occurs native in white, prismatic, or octohedral crystals; it is also found in combination with carbonate of lead. When procured artificially, it forms a white powder, slightly soluble in nitric acid, considerably so in a solution of acetate of ammonia of sp. gr. 1.066, or upwards. The other salts of ammonia possess the same property, but to a smaller extent. They form double salts with the sulphate of lead, and these compounds are slightly soluble. Sulphate of lead dissolves also, to some extent, in concentrated sulphuric acid, but it is insoluble in pure water. It may be obtained by adding sulphuric acid, or a solution of any sulphate, to a solution of one of the salts of lead. Like all the insoluble compounds of this metal, it is gradually decomposed by sulphuretted hydrogen; a black sulphide of lead is formed, and the acid is set free. Before the blowpipe it yields metallic lead in the reducing flame.

(765) *Nitrates of Lead*.—Oxide of lead combines with nitric acid in several proportions, viz.:  $\text{PbO}$ ,  $\text{NO}_5$ ; 2  $\text{PbO}$ ,  $\text{NO}_5$ ; 3  $\text{PbO}$ ,  $\text{NO}_5$ , and 6  $\text{PbO}$ ,  $\text{NO}_5$ .

*Nitrate of Lead* ( $\text{PbO}$ ,  $\text{NO}_5$ ), *Eq.* 165.57. —This salt is easily formed by dissolving litharge or metallic lead in excess of nitric acid somewhat diluted; it crystallizes in regular anhydrous octohedra, which are sometimes transparent, but more commonly milk white and opaque. It is soluble in about 8 parts of cold water, and insoluble in alcohol. If heated to redness, it fuses and is decomposed; oxygen, and peroxide of nitrogen ( $\text{NO}_2$ ), in the anhydrous state, are evolved (309), while protoxide of lead remains. Caustic ammonia if added to a solution of the nitrate, in quantity insufficient to combine with the whole of the acid, throws down a sparingly soluble *dinitrate of lead* (2  $\text{PbO}$ ,  $\text{NO}_5$ ). This salt may be also procured by boiling the neutral nitrate with litharge. It is deposited

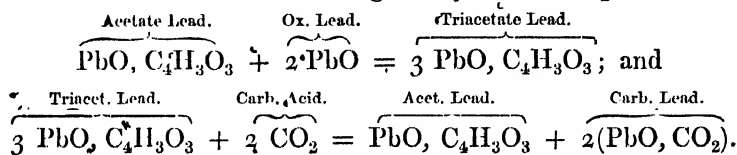
from its solution in hot water, in small opaque anhydrous crystals, which decrepitate forcibly when heated. By precipitating the nitrate with a slight excess of ammonia, a *trinitrate* is formed, which falls as a white powder, containing  $1\frac{1}{2}$  equivalents of water; by adding a large excess of ammonia to the neutral nitrate, a *hexanitrate* is formed; it also contains  $1\frac{1}{2}$  equivalents of water (Berzelius).

(766) *Nitrites of Lead*.—The action of metallic lead on a solution of the nitrate of lead is remarkable; the acid of the neutral salt imparts oxygen to the metal, which is dissolved, whilst subsalts of the lower oxides of nitrogen are produced. Several of these compounds may be obtained; the composition of the subsalt varying according to the proportions of the neutral nitrate and of the metal employed. When a solution of 166 parts or 1 equivalent of nitrate of lead, is heated to about  $140^{\circ}$  F., with 104 parts or 1 equivalent of metallic lead, perfect solution takes place, and a salt having the formula  $(2 \text{ PbO}, \text{NO}_2, \text{aq})$ , crystallizes on cooling in yellow plates; for  $\text{PbO}, \text{NO}_2 + \text{Pb} = 2 \text{ PbO}, \text{NO}_2$ . If  $1\frac{1}{2}$  equivalent of lead be employed instead of 1 equivalent, another salt, composed of  $(7 \text{ PbO}, \text{HO}, \text{NO}_2, 2 \text{ aq})$  crystallizes in heavy orange-red needles. By boiling a very dilute solution of the nitrate with 2 equivalents of lead for some time, a third salt, which is a *tetra-nitrite of lead*, composed of  $(4 \text{ PbO}, \text{NO}_2, \text{aq})$  (Peligot), crystallizes in hard rose-red silky needles, which are but sparingly soluble in hot water, and still less so in cold: a neutral nitrite of lead,  $\text{PbO}, \text{NO}_2$ , and a bibasic nitrite,  $2 \text{ PbO}, \text{NO}_2, \text{HO}$ , as well as a tribasic nitrite,  $3 \text{ PbO}, \text{NO}_2$ , have also been formed.

(767) *Phosphates of Lead*.—The salts of lead give a white precipitate with each modification of phosphoric acid; they are principally interesting as furnishing an easy means of procuring the hydrates of these different acids, by suspending the corresponding salt in water, and decomposing it by means of a current of sulphuretted hydrogen. All the phosphates of lead are soluble in nitric acid. The *Diphosphate of lead*  $(2 \text{ PbO}, \text{PO}_5)$ , before the blow-pipe, furnishes a semi-transparent globule, which becomes remarkably crystalline on cooling. *Triphosphate of lead* occurs both massive, and crystallized in 6-sided prisms; the produce of a small mine at Wissembourg consists principally of this compound, mixed with the carbonate of lead. A *chlorophosphate of lead*,  $\text{PbCl} + 3(3 \text{ PbO}, \text{PO}_5)$ , is found native in yellow 6-sided prisms.

*Boracic acid* may be fused with oxide of lead in all proportions; borate of lead enters into the composition of Faraday's optical glass.

(768) *Carbonate of Lead, or White Lead.*—Several methods are adopted in the manufacture of this compound: in all of them, however, certain peculiarities in the properties of the acetates of lead are taken advantage of. There are two acetates of lead, a neutral salt,  $\text{PbO}, \text{C}_4\text{H}_3\text{O}_3$ , and a tribasic acetate,  $3 \text{PbO}, \text{C}_4\text{H}_3\text{O}_3$ . A solution of the neutral acetate in the presence of an excess of oxide of lead readily unites with it to form the basic salt, and this subacetate, if exposed to an atmosphere containing carbonic acid, rapidly absorbs this gas, and is thus converted into carbonate of lead and neutral acetate. These changes may be thus represented:—



Two principal methods are in use for making white lead: the following is the plan which is known as the Dutch method; it is still carried on extensively at Lille:—A number of small glazed earthen pots are partially filled with a weak malt vinegar, and in each pot a thin sheet of lead coiled into a spiral form is placed; these pots are each covered with a plate of lead, and arranged in rows; they are then placed in tiers one above another to a depth of 18 or 20 feet, and imbedded in decomposing horse-dung; the warmth given out during its putrefaction volatilizes the vinegar, and under the united influence of the air and acid fumes, an oxide of lead is formed upon the surface of the coils of metal; this oxide combines with the acetic acid which rises in vapour from the vinegar, and a basic acetate of lead is thus produced. The carbonic acid which is supplied from the decomposing hot-bed readily converts this salt into carbonate of lead and the neutral acetate; whilst the neutral acetate again combines with a fresh portion of newly formed oxide, and produces the subacetate, which is decomposed as before: successive decompositions and recompositions ensue, as the neutral acetate immediately dissolves any oxide of lead presented to it, forming the subacetate, which again is decomposed under the influence of carbonic acid.

Since the lead in this process derives oxygen from the air, it is necessary that the atmosphere be allowed to come sufficiently into contact with the coils. The quantity of vinegar which is required is very small, 1 part of pure acetic acid to 100 parts of lead being amply sufficient. The carbonate is thus produced very slowly, and forms a compact layer upon the surface of the coils. It

always contains an excess of hydrated oxide of lead, but the proportion of this oxide is liable to vary. Mulder found a specimen which he examined to contain  $\text{PbO}, \text{HO} + 3 (\text{PbO}, \text{CO}_2)$ ; but more usually it consists of  $\text{PbO}, \text{HO} + 2 (\text{PbO}, \text{CO}_2)$ . By unrolling the coils, the carbonate breaks off in flakes of a dead white colour, furnishing the kind of white lead most approved by artists and colourmen. Before it is fitted for their use, it is subjected to the processes of grinding and levigation, by which it is reduced to an impalpable powder. Although this pulverization is performed under water, the fine particles of the carbonate become diffused through the air, rendering the operation very deleterious to the workmen. This circumstance, combined with the length of time requisite for the formation of the carbonate, induced Thénard to substitute for the foregoing process the direct decomposition of a solution of the subacetate of lead, by means of a current of carbonic acid: the carbonate is thus procured in a state of extreme division, and as rapidly as can be desired: it is, however, of a less opaque white, owing to its being deposited in exceedingly minute crystals, and is considered of a quality inferior to that procured by the Dutch method.

A third process, at one time employed at Birmingham, consisted in exposing litharge, moistened with a solution of acetate of lead, to a current of impure carbonic acid, obtained from the combustion of coke.

Carbonate of lead is often fraudulently mixed with a considerable quantity of sulphate of baryta, which is much cheaper, though its whiteness is less intense; a small quantity of indigo, charcoal, or sulphide of lead is usually added to white lead, in order to substitute a bluish tint for the natural tendency of the white towards yellow.

(769) CHARACTERS OF THE COMPOUNDS OF LEAD.—The salts of lead are colourless. They have a poisonous action on the system. In cases of poisoning by a dose of the soluble salts of lead, the best antidote is sulphate of magnesia, or of soda, which forms an insoluble and inert sulphate of lead. This, however, is of no avail in the more usual forms of lead poisoning, in which the metal is introduced in minute quantities unintentionally, in water, or in articles of diet.

The best tests for lead are the formation of a white insoluble sulphate when *sulphuric acid* or the *sulphates* are added to its solutions; a black sulphide with *sulphuretted hydrogen*; a yellow chromate with *chromate of potash*; and a yellow iodide with *iodide of potassium*. Potash gives a white precipitate of the hydrated

oxide, which is redissolved in an excess of the alkalies. *Carbonate of potash*, or of *soda*, gives a dense white precipitate of white lead. Many other insoluble white salts may be formed, as the phosphate, arseniate, and the ferrocyanide. Lead has a remarkable tendency to form subsalts, but the number of its double salts is not great. From the insolubility of many of its organic compounds, it has been much used to determine the combining proportion of organic bodies. It is, however, more advantageous to employ the oxide of silver for this purpose, as the oxide of lead is to a small extent volatile.

Lead, like most other metals of comparatively weak affinity for oxygen, is easily precipitated from its solutions in the metallic state by the metals more oxidable than itself: if, for instance, a piece of zinc be suspended in a solution containing lead, crystals of lead are deposited in a beautiful arborescent form.

*Before the blowpipe* on charcoal the salts of lead yield a soft white malleable bead of the metal, surrounded by a yellow ring of oxide.

(770) *Estimation of Lead*.—Lead is generally estimated in the form of the sulphate, which contains 68.31 per cent. of the metal. More rarely it is determined from the protoxide, of which 100 parts correspond to 92.82 of lead; porcelain crucibles must be employed for these experiments, as oxide of lead is easily reduced to the metallic state, in which case it would form an alloy with platinum, and would ruin a crucible composed of this metal.

Lead may be separated by means of sulphuric acid from all the metals, except its insoluble combinations with the metallic acids. The following is the method to be adopted:—If a galena or an alloy of lead is to be analysed, it should be treated with concentrated nitric acid until it is completely decomposed, and then evaporated nearly to dryness with a small excess of sulphuric acid; the nitric acid is thus expelled, and the metals are converted into sulphates; the mass is treated with water, which dissolves out all the metals except lead, tin, and antimony: quartz, or sulphate of baryta, if present, would also be contained in this insoluble portion. The insoluble residue is collected and weighed, and then digested repeatedly in a solution of acetate of ammonia, of sp. gr. 1.065: after which the residue is again washed, dried, and weighed: the difference indicates the proportion of sulphate of lead which is dissolved out from the oxides of antimony and tin, and from the quartz and sulphate of baryta. The lead may be obtained from its solution in the acetate of ammonia by the addition of hydrosulphate of ammonia: and the sulphide of lead thus precipitated may be converted into sulphate by means of a mixture of nitric and sul-

phuric acids. It is evaporated down to dryness, ignited, dried, and weighed.

The salts of lead with the metallic acids may be decomposed by fusing them with a mixture of caustic potash and carbonate of potash: the metallic acid combines with the potash, and may be dissolved by the addition of water, whilst the oxide of lead is left.

## CHAPTER XVII.

### GROUP VII.—THE NOBLE METALS.

#### § I. MERCURY.

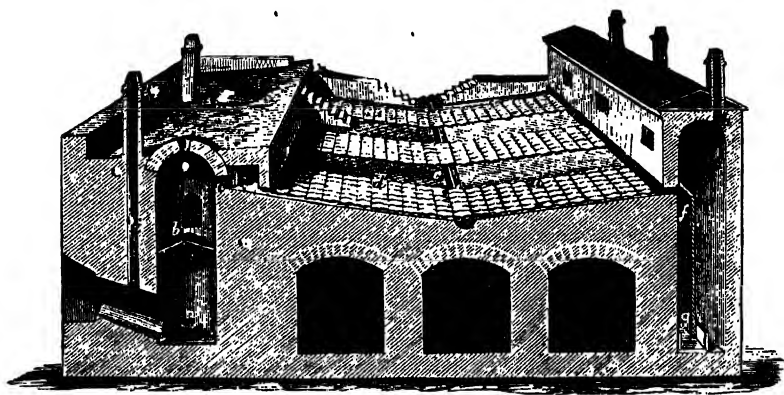
*Symbol*, Hg; *Equivalent*, 100; *Specific Gravity as liquid at 32° F.*, 13.596; *Sp. Gr. as vapour*, 6.976; *Combining Volume*, 2.

(771) MERCURY or *Quicksilver* is one of the metals which have been longest known; it is found in but few localities, and occurs most frequently in the form of the sulphide (cinnabar), usually accompanied with small quantities of the metal in its native state. Occasionally it is met with combined as an amalgam with silver, and sometimes in the form of subchloride or calomel. Generally speaking, its ores are found in clay slate or in the red sandstone underlying the coal, and not unfrequently among the coal measures themselves. The most productive mines are those of Almaden, in Spain; very extensive and valuable deposits of cinnabar have likewise been lately found in California; and the mines of Idria, in Transylvania, have also been extensively worked. Considerable quantities are likewise raised in China and Japan, and from the mine of Huancavelica, in Peru. Experience has shown that unless the ore contain at least  $\frac{1}{10}$ th its weight of this metal, or about 3.8 lb. per ton, it is too poor to be wrought with advantage by the methods now in use.

*Extraction*.—The metal may be obtained from its ore either by burning off the sulphur and distilling the mercury,—a process which applies both to cinnabar and to the native metal; or by heating the cinnabar with some substance capable of combining with the sulphur, and forming a fixed compound, from which the mercury is separated by heat. At Almaden, the metal is extracted by the first process. Fig. 311 shows a section of the furnace employed: each furnace contains two grates, and on the lower

one, *a*, provided with a chimney, *i*, a fire of brushwood is kindled; the upper grating is formed by a brick arch, *b*, perforated with numerous apertures; on this arch the sulphide rests, the poorer pieces of ore being placed at the bottom. The brushwood quickly kindles the sulphur in the ore, which afterwards, by its combustion maintains sufficient heat to continue the operation without the use of any other fuel: sulphurous acid is formed, and the liberated mercury distils, and is condensed in wide earthen pipes, *d d*, connected with the upper aperture, *c*, of the

FIG. 311.



furnaces; these pipes are termed *aludels*. The aludels are supported on a doubly inclined plane of masonry; at the lowest point a perforation is made to allow of the escape of the mercury into a brick channel, *e*, through which it runs into a well; the further end, *f*, of the aludels opens into a condensing chamber, in which an additional quantity of mercury is deposited in the trough, *g*: the sulphurous acid escapes into the air, through the chimney, *h*. Great waste, however, is incurred during this process from the incomplete manner in which the condensation is effected. A better plan consists in mixing the sulphide with iron filings, or, as is more commonly done, with slacked lime, and conducting the distillation in cast-iron furnaces and retorts. The mercury is condensed in receivers partly filled with water, while sulphide of calcium and sulphate of lime remain behind in the retort:  $4 \text{HgS} + 4 \text{CaO} = 4 \text{Hg} + 3 \text{CaS} + \text{CaO}, \text{SO}_3$ .

If the ore contain any admixture of zinc and bismuth, small portions of these metals are liable to be distilled over with the mercury. In this case a film forms upon the surface of the fluid metal

when it is agitated in contact with air. The purity of the product is easily seen by the absence of this film, and by the perfect mobility and sphericity of the globules, which do not wet the surface of non-metallic objects. A small quantity of mercury may be speedily purified by placing it in a bottle, with a little finely powdered loaf sugar; the mercury should not occupy more than one-fourth of the capacity of the bottle: the bottle is then closed, and briskly agitated for a few minutes; after which the stopper is withdrawn, and fresh air is blown into the bottle with a pair of bellows, and the agitation is repeated: this is done 3 or 4 times, and the mercury is then poured into a cone of smooth writing paper, in the apex of which a pin hole is made; the metal runs through, and leaves the powdered sugar mixed with the oxides of the foreign metals, and a considerable quantity of finely divided mercury.

Generally speaking, the mercury imported into this country is almost chemically pure. Any foreign metals which may be present in it may be removed by digesting it for some days with dilute nitric acid in the cold: the mercury should be placed in a shallow dish, so as to expose a large surface to the acid, and it should be frequently agitated; the acid exerts but little action on the mercury so long as any more oxidizable metals are present. A solution of nitrate of mercury may be substituted for the nitric acid with advantage; in this case the mercury is deposited from the solution and takes the place of the other metals, which are dissolved.

(772) *Properties*.—Mercury possesses a lustre resembling that of polished silver. It is the only metal that is fluid at common temperatures. It freezes at  $-39^{\circ}$  F., and contracts considerably at the moment of congelation, when it crystallizes in octohedra. In this state it is malleable; when heated to  $662^{\circ}$  F. it boils, and forms an invisible, transparent vapour, of sp. gr. 6.976 (Dumas). The metal, at all temperatures above  $40^{\circ}$ , undergoes slight spontaneous evaporation. Its specific gravity at  $60^{\circ}$  is 13.54. When pure, it is not tarnished by exposure to air and moisture at ordinary temperatures, but if heated to about  $700^{\circ}$  or  $800^{\circ}$  F. it absorbs oxygen, and is gradually converted into the red oxide. Hydrochloric acid is without action upon the metal, either when cold or hot. Concentrated sulphuric acid in the cold produces no change, but when heated with it is decomposed; sulphurous acid being evolved, while the mercury is oxidized and combines with a portion of undecomposed acid. Strong nitric acid dissolves it with rapidity, extricating deutoxide of nitrogen in abundance, while nitrate of mercury is formed. If the acid be dilute, and the metal in excess,



the mercury is dissolved slowly, and at ordinary temperatures the nitrate of the suboxide is the result.

Mercury may be obtained in a state of extreme division, by precipitating a solution of corrosive sublimate, by means of the solution of protochloride of tin. The chloride of tin, if added in sufficient quantity, absorbs all the chlorine, and a grey metallic powder subsides;  $\text{HgCl} + \text{SnCl} = \text{Hg} + \text{SnCl}_2$ .

*Uses.*—Mercury is employed extensively in the extraction of gold and silver from their ores, by the processes of amalgamation; great quantities are annually sent to South America for this purpose. Its amalgams are largely employed in the processes of silvering and gilding. Mercury is also used in the preparation of vermilion, which is highly valued as a pigment, for the purity and permanence of its tint. It is indispensable in the construction of philosophical instruments; and it is well known in various forms as an invaluable medicine. By trituration with saccharine, or oleaginous substances, it admits of being minutely subdivided, and a small portion of it becomes oxidized, to which the active properties of blue pill appear to be owing: the same remark applies to the mercurial ointment, and the *pulvis hydrargyri cum cretâ*.

(773) *Oxides of Mercury.*—Mercury forms two oxides, the black suboxide,  $\text{Hg}_2\text{O}$ , and the red oxide,  $\text{HgO}$ : both of them form salts with acids.

The *Suboxide of Mercury* ( $\text{Hg}_2\text{O}$ , *Eq.* 208, *Sp. Gr.* 10.68), though a powerful saline base, is very unstable when isolated. It is best procured by triturating finely levigated calomel with solution of potash or of soda, and washing the black precipitate thus obtained with cold water. It must be allowed to dry spontaneously in a dark place; even when dry, mere exposure to light, or a very gentle heat, is sufficient to convert it into red oxide and the metal.

(774) *Nitric Oxide, or Red Oxide of Mercury* ( $\text{HgO}$ ), *Eq.* 108, *Sp. Gr.* 11.29.—This oxide may be obtained in red scales by heating metallic mercury to  $700^\circ$  or  $800^\circ$  in a matrass: but this process is very slow, and not productive: it is more conveniently prepared by the decomposition of the nitrate by heat, and it then has a bright orange colour. It may also be thrown down in the form of a yellow powder, when potash or soda is added to a solution of corrosive sublimate, or of nitrate of mercury. The precipitated oxide does not differ in composition from the red crystallized form, but it enters more readily into combination; oxalic acid is without

action on the crystallized oxide, but it converts the precipitated oxide into oxalate, and the yellow oxide when boiled with solution of corrosive sublimate, is quickly converted into the oxychloride; but this change is very slow with the crystallized variety. The yellow oxide, when boiled with bichromate of potash, yields a subchromate of mercury,  $3 \text{ HgO}, \text{CrO}_3$ ; but the crystallized oxide, when similarly treated, yields subsalt with a larger excess of base,  $4 \text{ HgO}, \text{CrO}_3$  (Millon). In short, the crystallized oxide obtained by the direct oxidation of mercury and the precipitated oxide appear to be different allotropic modifications of the compound.

The red oxide when heated becomes nearly black, but recovers its colour on cooling; when exposed to a temperature of ignition, it is decomposed into metallic mercury and oxygen gas. It is slightly soluble in water; the solution has an acid taste, and turns syrup of violets green. This oxide of mercury forms with baryta a soluble compound. With ammonia, a yellowish-white insoluble mass ( $4 \text{ HgO}, \text{H}_3\text{N}, 2 \text{ H}_2\text{O}$ ) is produced. It enters into combination with acids, and forms well defined salts. It may be provisionally distinguished as *mercuramine*.

(775) *Mercuramine* ( $4 \text{ HgO}, \text{H}_3\text{N}, 2 \text{ H}_2\text{O}$ ) or ( $2 \text{ HgO}, \text{Hg}_2\text{H}_2\text{N}$ )  $\text{O}, 2 \text{ H}_2\text{O}$ .—When a solution of ammonia is poured upon yellow precipitated oxide of mercury in a bottle which admits of being closed, to prevent the access of carbonic acid from the air, the colour of the oxide becomes paler, and eventually a yellowish-white amorphous powder is obtained, which, when washed and dried in a dark place, over quick-lime, forms a hydrate of a new basic substance, containing  $4 \text{ HgO}, \text{H}_3\text{N}, 2 \text{ H}_2\text{O}$ . This compound was discovered by Fourcroy and Thénard, but it was first completely examined by Millon (*Ann. de Chimie*, III., xviii. 393). In its isolated condition, it is very unstable: mere exposure to the light decomposes it. When triturated in a mortar, it produces a series of small detonations. If dried in vacuo over sulphuric acid, it loses two equivalents of water; and between  $212^\circ$  and  $266^\circ$ , a third equivalent of water is expelled: it thus becomes dark brown, and is permanent in the air. These changes may be thus explained: 1 equivalent of ammonia and 2 of water, in acting upon 4 equivalents of oxide of mercury, produce the yellowish hydrated compound,  $4 \text{ HgO}, \text{H}_3\text{N}, 2 \text{ H}_2\text{O}$ . The 2 equivalents of water are removed by desiccation over sulphuric acid, and on the application of heat, 1 equivalent of the hydrogen of the ammonia removes an equivalent of oxygen, whilst the amidogen takes its place;  $4 \text{ HgO}, \text{H}_3\text{N} = 3 \text{ HgO}, \text{HgH}_2\text{N} + \text{H}_2\text{O}$ .

Mercuramine is a powerful base; its terhydrate absorbs car-

bonic acid from the air almost as rapidly as slaked lime. It is insoluble in water or in alcohol, but it decomposes solutions of the salts of ammonia and combines with the acid. Definite salts with sulphuric, nitric, oxalic, carbonic, hydrochloric, and various other acids have been formed. On the addition of soda or potash to the solutions of these salts, the hydrate of the base is precipitated. The formula of the sulphate is  $(2 \text{ HgO}, \text{Hg}_2\text{H}_2\text{N}) \text{O}, \text{SO}_3$ ; that of the chloride,  $(2 \text{ HgO}, \text{Hg}_2\text{H}_2\text{N}) \text{Cl}$ . It may be obtained as a yellow precipitate, by adding solution of corrosive sublimate to a solution of ammonia in excess, and washing the precipitate with boiling water (781).

(776) *Sulphides of Mercury*.—The two sulphides of mercury,  $\text{Hg}_2\text{S}$ , and  $\text{HgS}$ , correspond in composition to the oxides and chlorides.

The *Subsulphide of Mercury* ( $\text{Hg}_2\text{S}$ , *Eq.* 216), is scarcely more stable than the suboxide of the metal; it is procured by transmitting a current of sulphuretted hydrogen through a solution of a mercurial subsalt, or by triturating 16 parts of moistened sulphur with 200 of mercury; it forms a black powder, which was formerly termed *Ethiops mineral*. It is decomposed by nitric acid, and if the dry sulphide be sublimed, it is converted into cinnabar and metallic mercury.

(777) *Sulphide of Mercury, or Cinnabar* ( $\text{HgS}$ , *Eq.* 116; *Sp. Gr.* 8.2), is the most abundant ore of mercury. This compound occurs sometimes crystallized in hexahedral prisms, but more usually as a fibrous or amorphous mass, and is a product of considerable importance in the arts, forming the pigment known under the name of vermilion. Some portions of the native cinnabar are of a sufficiently delicate colour to be employed after mere levigation; but it is usually prepared artificially. In Holland, this manufacture is carried on to a considerable extent. The process adopted consists in triturating sulphur with about 6 times its weight of mercury, aiding the action by a gentle heat. The black mass thus procured is thrown (in successive portions, to prevent too rapid an action) into tall earthen pots, the lower parts of which have been previously brought to a red heat; the aperture at top is closed with an iron plate, and in about 32 hours after the introduction of the whole charge, the sublimation is complete: when cold, the pots are broken, and the cinnabar, which is found deposited in layers upon the upper part, is carefully removed; the cinnabar is levigated with water, and the fine powder thus obtained is sold as vermilion; an excess of sulphur is to be avoided,

as it impairs the brilliancy of the colour. Cinnabar forms a yellowish-brown vapour, of a sp. gr. of 5.51. Vermilion may also be procured in the wet way, but the process is tedious, and less certain. The Chinese vermilion is supposed by some chemists to be prepared by the humid process. In order to produce vermilion in this manner, M. Brunner recommends 100 parts of mercury to be triturated, for 2 or 3 hours, with 38 parts of sulphur; at the end of which time, 25 parts of caustic potash and 150 parts of water are to be added. The mixture is maintained for some hours at a temperature of from  $112^{\circ}$  to  $120^{\circ}$  F., at first stirring it constantly: the black colour gradually changes to scarlet; as soon as it has attained the desired tint, it is thoroughly washed with cold water. If the heat be too long continued, the tint changes to brown, but the scarlet hue is restored by boiling it with water.

Sulphide of mercury is thrown down as a black precipitate by transmitting sulphuretted hydrogen through solutions of the persalts of mercury: when dried and sublimed, it assumes its ordinary red colour. The pure acids are without action upon it, but it is oxidized and dissolved by aqua regia. The alkalis in solution do not decompose cinnabar, but if ignited with it in the dry state, a sulphate and sulphide of the alkaline metal are formed, and metallic mercury sublimes;  $4 \text{ HgS} + 4 \text{ KO} = 4 \text{ Hg} + \text{K}_2\text{O} + \text{SO}_3 + 3 \text{ KS}$ . Sulphide of mercury possesses the property of uniting with other metallic sulphides; it also combines with the nitrate, the chloride, the iodide, and some other mercurial salts, forming peculiar compounds, which are produced by the action of a small proportion of sulphuretted hydrogen upon the solutions of these salts, and cause the first portions of the precipitate occasioned in them by the gas to assume a white colour.

(778) *Chlorides of Mercury*.—Mercury forms two chlorides, a subchloride,  $\text{Hg}_2\text{Cl}$ , well known as calomel, and a chloride,  $\text{HgCl}$ , commonly distinguished as corrosive sublimate.

*Subchloride of Mercury* ( $\text{Hg}_2\text{Cl}$ ), *Eq.* 235.5; *Sp. Gr.* 7.178.—*Calomel* may be obtained by precipitating the subnitrate of mercury by means of a solution of common salt; but it is more usually procured by sublimation: 13 parts of mercury are triturated with 17 of corrosive sublimate, until no metallic globules are visible, the chloride having been previously moistened with water or alcohol to prevent the acrid particles from being diffused through the air; the mixture is then sublimed in suitable vessels, and the calomel is deposited as a semi-transparent fibrous cake. In this operation the additional mercury combines with half the chlorine of

the chloride;  $\text{HgCl} + \text{Hg} = \text{Hg}_2\text{Cl}$ . Sometimes the vapours are sent into a capacious chamber; the deposit then assumes the form of a fine powder. Calomel requires careful washing and levigation, because portions of the undecomposed chloride always sublime with the calomel, and they can only be removed by repeated washing. It was formerly supposed that the medical character of calomel was rendered milder by repeated sublimations. This, however, has been found to be a serious mistake, as every time that calomel is sublimed, a small portion is reconverted into corrosive sublimate and metallic mercury.

Calomel sublimes in quadrilateral prisms, terminated by 4-sided pyramids; when powdered it is of a yellowish-white colour. It begins to sublime below redness, and before undergoing fusion. Calomel is tasteless and insoluble in water; the alkalies decompose it. Soda and potash set free the protoxide. Solution of ammonia forms with it a black compound, consisting of  $\text{Hg}_2\text{Cl}$ ,  $\text{Hg}_2\text{H}_2\text{N}$ : this change is explained in the subjoined equation;  $2\text{Hg}_2\text{Cl} + 2\text{H}_3\text{N} = \text{Hg}_2\text{Cl}$ ,  $\text{Hg}_2\text{H}_2\text{N} + \text{H}_4\text{NCl}$ . Sulphuric acid is without action on calomel; boiling nitric acid dissolves it, and forms corrosive sublimate and nitrate of mercury; if boiled for a long time with hydrochloric acid or chloride of sodium, it is resolved into corrosive sublimate and metallic mercury: the same effect is produced, but more rapidly, by boiling it in solution of sal ammoniac.

(779) *Chloride of Mercury; Corrosive Sublimate* ( $\text{HgCl}$ ), *Eq.* 135.5; *Sp. Gr.* 6.223.—When heated mercury is placed in an atmosphere of chlorine it ignites from the rapid union of the gas with the metal, and the chloride is formed. It is prepared on the large scale by mixing intimately  $2\frac{1}{2}$  parts of sulphate of mercury with 1 part of common salt, and subliming the mixture in glass vessels at a carefully regulated heat; sulphate of soda remains in the vessel, and the chloride sublimes, as represented in the equation  $\text{HgO}$ ,  $\text{SO}_3 + \text{NaCl} = \text{NaO}$ ,  $\text{SO}_3 + \text{HgCl}$ . The fumes are extremely acrid and poisonous. Corrosive sublimate fuses and boils before undergoing sublimation; its vapours are condensed in snow-white crystalline needles, or in octohedra with a rectangular base. It has an acrid burning taste, and disgusting metallic flavour. It is soluble in 16 parts of cold water, and in less than 3 of boiling water; on cooling it is deposited from a concentrated solution in transparent anhydrous quadrilateral prisms. Its solution, by long exposure to light, is gradually decomposed, and calomel is deposited. Cold alcohol dissolves nearly one-third of its weight of the salt, and an equal weight when boiling; ether also

dissolves it freely. If an aqueous solution be agitated with ether, almost the whole of the salt will be abstracted by it from the water, and the ethereal solution will rise to the surface. It is very soluble in solutions of the alkaline chlorides, with which it enters into combination, forming double salts. With chloride of potassium it forms three distinct crystallizable compounds,  $\text{KCl}, 4 \text{HgCl}$ , 4 aq;  $\text{KCl}, 2 \text{HgCl}$ , 2 aq; and  $\text{KCl}, \text{HgCl}$ , aq. They are easily prepared by dissolving the salts in the proper proportions, and allowing them to crystallize. With chloride of sodium only one such compound is formed,  $\text{NaCl}, 2 \text{HgCl}$ , 3 aq. A salt of ammonia with 3 equivalents of sal ammoniac has long been known as *sal alembroth*: it crystallizes in flattened rhomboidal tables.

Similar compounds having a composition analogous to that of the sodium salt may be formed with most of the soluble chlorides. Chlorides of calcium and magnesium form more than one compound. A similar but anhydrous salt,  $\text{HCl}, 2 \text{HgCl}$ , is formed by dissolving corrosive sublimate in hot hydrochloric acid, from which it crystallizes on cooling; it is, however, decomposed by water.

Chloride of mercury combines with the sulphide, and forms with it a white insoluble gelatinous compound, consisting of  $2 \text{HgS}, \text{HgCl}$ ; it is the white precipitate which is always formed at first, on passing a current of sulphuretted hydrogen through a solution of corrosive sublimate.

Corrosive sublimate is decomposed by the fixed alkalis and alkaline earths; a chloride of the alkaline metal is formed, and oxide of mercury is set free. When ammonia is added to a solution of corrosive sublimate, it separates only half the chlorine, uniting with the remainder to form the compound called white precipitate. Chloride of mercury acts powerfully on the albuminous tissues, and combines with them; it is a violent and acrid poison. The best antidote in cases of poisoning with this substance is the immediate exhibition of the whites of several raw eggs, as it coagulates the albumen, and forms with it a sparingly soluble compound. It was supposed that the chloride was converted into calomel, but this does not appear to be the case.

(78c) Corrosive sublimate combines with oxide of mercury in at least 3 proportions. One of these is obtained in the form of dark brown insoluble flakes,  $(3 \text{HgO}, \text{HgCl})$ , when the chloride is boiled with red oxide of mercury; these compounds are decomposed by the alkalis.

The oxychlorides of mercury are interesting, from the observations of Millon upon them, which seem to prove the persistence

of the allotropic modification in a body after it has entered into combination.

The three oxychlorides described by Millon consist of ( $\text{HgCl}$ , 2  $\text{HgO}$ ), ( $\text{HgCl}$ , 3  $\text{HgO}$ ), and ( $\text{HgCl}$ , 4  $\text{HgO}$ ). They may all be produced by the action of bicarbonate of potash upon a solution of corrosive sublimate. The first may be obtained in three different isomeric conditions, the second in two, and the third in three. The action of the carbonates of ~~the~~ alkalis upon solutions of corrosive sublimate is peculiar. The addition of solution of sublimate to a solution of pure *neutral* carbonate of soda or potash is attended with the precipitation of yellow oxide of mercury. If the mercurial solution be added to a solution of an alkaline *bicarbonate*, a red oxychloride is formed; and if even a small quantity of bicarbonate of the alkali be mixed with a large proportion of neutral alkaline carbonate, this red precipitate is produced at first. This reaction may serve to indicate the difference between carbonates and bicarbonates in solution. If a cold saturated solution of bicarbonate of potash be added gradually to 8 or 10 times its volume of a cold saturated solution of sublimate, a light granular amorphous precipitate of a bright brick-red colour is formed ( $\text{HgCl}$ , 2  $\text{HgO}$ ). If the volume of the solution of sublimate be only 3 or 4 times as great as that of the bicarbonate, a precipitate of similar composition is formed, but it is dense, crystalline, and red, purple, or violet, in colour. Both these modifications, when decomposed by potash, yield the *yellow oxide* of mercury, but if 1 volume of the solution of bicarbonate be added to 2 volumes of the solution of sublimate, stirring briskly, a jet black crystalline precipitate is formed, which also consists of  $\text{HgCl}$ , 2  $\text{HgO}$ , but which yields the *red crystalline oxide* when decomposed by potash.

If equal volumes of the solutions be mixed, golden-yellow plates, which gradually become brown or yellowish, are deposited, ( $\text{HgCl}$ , 3  $\text{HgO}$ ). The same body may also be obtained in the amorphous form.

The quadribasic oxychloride ( $\text{HgCl}$ , 4  $\text{HgO}$ ) may be obtained by adding a solution of corrosive sublimate to a large excess of the solution of the bicarbonate. Carbonic acid gradually escapes and brown crystalline crusts are deposited: caustic potash causes the separation of the *red oxide* of mercury from this compound. This oxychloride may also be obtained in the form of a brown amorphous deposit; and in golden-yellow plates; both these varieties yield the *yellow oxide* when decomposed by potash. The first two oxychlorides are converted by boiling them with water into the quadribasic form, which is deposited from the solution in golden yellow scales.

(781) *Action of Ammonia on Chloride of Mercury.*—When a solution of corrosive sublimate is added to a solution of ammonia in excess, one half of the chlorine only is removed from the salt, and a *white precipitate* is formed, which, when washed with cold water, is completely soluble in nitric and hydrochloric acids, and which therefore can contain no calomel;  $2 \text{HgCl} + 2 \text{H}_3\text{N} = (\text{HgCl}, \text{HgH}_2\text{N}) + \text{H}_4\text{NCl}$ . Kane considers this white precipitate as a compound of chloride with amide of mercury,  $\text{HgCl}, \text{HgH}_2\text{N}$ ; but it may also be regarded as chloride of ammonium, in which 2 equivalents of hydrogen are displaced by 2 equivalents of mercury ( $\text{Hg}_2\text{H}_2\text{N}, \text{Cl}$ ). If ammonia be added drop by drop to a solution of corrosive sublimate, which is purposely maintained in considerable excess, the precipitate consists of 3  $\text{HgCl}, \text{HgH}_2\text{N}$ , or chloride of mercuramine, in which the place of the oxygen is supplied by chlorine.

White precipitate has been made the subject of numerous experiments. If it be heated to about  $600^\circ \text{F}$ ., ammonia, and the ammoniated chloride of mercury are expelled; and a red crystalline powder remains, represented by the formula,  $(2 \text{HgCl}, \text{Hg}_3\text{N})$ ; for  $6 (\text{H}_2\text{Hg}_2\text{N}, \text{Cl}) = 3 \text{H}_3\text{N} + (\text{H}_3\text{N}, 2 \text{HgCl}) + 2 (2 \text{HgCl}, \text{Hg}_3\text{N})$ . This red powder is insoluble in water or in dilute acids, but it is dissolved and decomposed by either boiling hydrochloric acid or oil of vitriol. It is interesting, as it appears to contain ammonia in which the 3 eqs. of hydrogen are displaced by 3 eqs. of mercury.

When white precipitate is boiled in water it is decomposed, and the heavy insoluble canary-yellow chloride of mercuramine is formed, whilst chloride of ammonium is formed in the solution;  $2 (\text{HgCl}, \text{HgH}_2\text{N}) + 2 \text{HO} = (2 \text{HgO}, \text{Hg}_2\text{H}_2\text{N})\text{Cl} + \text{H}_4\text{NCl}$ . This yellow powder is dissolved easily by dilute nitric or hydrochloric acid.

If a solution of corrosive sublimate be added gradually to a boiling solution of sal ammoniac and free ammonia, as long as the precipitate is redissolved by agitation, a compound crystallizes in rhombohedra on cooling; and the same substance is procured on boiling ordinary white precipitate in a solution of sal ammoniac. This compound fuses at a temperature of  $572^\circ$ , and is decomposed; boiling water extracts a large proportion of sal ammoniac from it, and leaves the canary-yellow powder above described. It is freely soluble in acids, even in acetic acid. Kane's analysis of this compound would allow of its being represented by the formula,  $(\text{HgCl}, \text{HgH}_2\text{N}) + (\text{H}_4\text{N}, \text{Cl})$ , or still more simply as  $\text{HgH}_3\text{N}, \text{Cl}$ . It is sometimes called *fusible white precipitate*.

When corrosive sublimate is exposed to a current of dry ammoniacal gas, it fuses with extrication of heat; 2 equivalents of the salt absorb 1 equivalent of ammonia,  $\text{H}_3\text{N}, 2 \text{HgCl}$ . This com-



pound may be sublimed without change, but it is decomposed by water. It is a true ammoniated chloride of mercury.

The following are the compounds, which result from the combined action of ammonia and heat upon corrosive sublimate:—

- (1) White precipitate . . . .  $\text{HgCl}, \text{HgH}_2\text{N}.$
- (2) Red crystalline compound . . .  $2 \text{HgCl}, \text{Hg}_3\text{N}.$
- (3) Chloride of mercuramine . . .  $(2 \text{HgO}, \text{Hg}_2\text{H}_2\text{N})\text{Cl}.$
- (4) Trichloride of mercuramine . .  $(2 \text{HgCl}, \text{Hg}_2\text{H}_2\text{N})\text{Cl}.$
- (5) Fusible white precipitate . . .  $\text{HgCl}, \text{HgH}_2\text{N} + \text{H}_4\text{NCl}.$
- (6) Ammoniated chloride of mercury  $2 \text{HgCl}, \text{NH}_3.$

Besides the double salts, of which one is—

- (7) Sal alembrothi . . . . .  $3 \text{H}_4\text{NCl}, \text{HgCl}, \text{aq}.$
- (8) And another is . . . . .  $\text{H}_4\text{NCl}, 2 \text{HgCl}.$

These remarkable compounds derive interest from their connexion with the theories which have been proposed respecting the nature of ammonia, ~~the~~ the consideration of which will be resumed when the alkaloids or organic bases are examined.

(782) *Iodides of Mercury*.—Mercury forms three iodides: a subiodide,  $\text{Hg}_2\text{I}$ ; a protiodide,  $\text{HgI}$ ; and an intermediate iodide ( $\text{Hg}_2\text{I}, \text{HgI}$ ) of a yellow colour, obtained by precipitating nitrate of mercury by means of iodide of potassium containing iodine in solution.

The *subiodide* ( $\text{Hg}_2\text{I}$ , *Eq.* 327) is a green powder insoluble in water, which is easily decomposed by exposure to light into mercury and the red iodide; the same change is effected by heating it gently with the soluble iodides or chlorides, or with hydriodic or hydrochloric acid. If heated suddenly it fuses and is sublimed unchanged; but if the temperature be raised gradually, it is decomposed into the red iodide and metallic mercury. It is easily formed by triturating 127 parts of iodine with 200 of mercury, moistening the mixture with a little alcohol; or it may be precipitated from a solution of any of the salts of the suboxide of mercury by adding a solution of iodide of potassium.

*Iodide of Mercury* ( $\text{HgI}$ , *Eq.* 227).—This beautiful compound may be obtained by triturating an equivalent of iodine with one of mercury, and subliming the mixture; but it is procured most easily by precipitating a solution of corrosive sublimate by means of a solution of iodide of potassium: the precipitate is soluble in an excess of either salt. The precipitate is at first salmon coloured, but it speedily becomes converted into a brilliant scarlet crystalline deposit. It fuses at about  $400^\circ$ , and sublimes in yellow rhombic tables; the yellow colour is changed to red by mere agitation, or by scratching of the crystals. Mr. Warrington has

shown that this change of colour depends upon a change in the molecular constitution of the salt, in consequence of which the rhomboidal crystals are converted into octohedra with a square base. Iodide of mercury is insoluble in water, but it is taken up freely by alcohol. With the soluble electro-positive iodides it forms crystalline double salts, and it is dissolved easily by solutions of chlorides of the metals of the alkalies, but it does not form crystallizable compounds with these chlorides. A fusible double chloride and iodide of mercury ( $\text{HgI}$ ,  $\text{HgCl}$ ) may be formed; and a soluble crystallizable compound ( $\text{HgI}$ ,  $2 \text{HgCl}$ ) may be obtained by saturating a boiling solution of corrosive sublimate with the red iodide of mercury, and allowing it to crystallize. Iodide of mercury also forms definite compounds with the oxide, and with the sulphide of the metal.

Two bromides, analogous to the chlorides of mercury may be formed; they yield corresponding double salts.

(783) *Nitride of Mercury*.—Plantamour states, that by transmitting a current of dry ammoniacal gas over the yellow oxide of mercury, precipitated from its salts by an alkali, and well dried at a temperature not exceeding  $300^{\circ} \text{F}$ ., water is formed and volatilized, whilst an anhydrous powder of a flea-brown colour is produced. It detonates powerfully when heated, or struck; the acids decompose it, forming salts of ammonia and mercury. Its probable composition is  $\text{Hg}_3\text{N}$ , as inferred from the mode of preparing it;  $3 \text{HgO} + \text{H}_3\text{N} = \text{Hg}_3\text{N} + 3 \text{H}_2\text{O}$ .

(784) *Sulphate of Mercury* ( $\text{HgO}$ ,  $\text{SO}_3$ ), *Eq. 148, Sp. Gr. 4.666*.—When 2 parts of mercury are gently heated with 3 of oil of vitriol, sulphurous acid is evolved, and subsulphate of mercury is procured; but if the heat be increased, and the distillation be carried to dryness, the sulphate is formed; sulphurous acid being extricated, whilst the mercury takes oxygen from the sulphuric acid;  $\text{Hg} + 2 \text{SO}_3 = \text{HgO}$ ,  $\text{SO}_3 + \text{SO}_2$ . It is a white crystalline powder, which is soluble in a solution of common salt, but is decomposed by pure water into an insoluble yellow subsalt, called *turpeth mineral*  $3 \text{HgO}$ ,  $\text{SO}_3$ , and a soluble supersalt, which crystallizes in deliquescent needles: the yellow subsalt is formed more rapidly if the sulphate be washed with boiling water. The neutral sulphate unites with sulphate of ammonia, and forms a crystallizable double salt.

(785) The *nitrates of mercury* are more numerous than those of any other metal. The *neutral subnitrate* is obtained by digesting metallic mercury in an excess of nitric acid diluted with 4 or 5 times its bulk of water: it crystallizes in transparent

prisms,  $\text{Hg}_2\text{O}$ ,  $\text{NO}_5$ , 2 aq; water decomposes it into an insoluble basic salt, and a soluble acid one. A soluble subnitrate, which is often mistaken for the neutral salt, crystallizes in large transparent prisms, and is obtained by digesting an excess of mercury in dilute nitric acid: its composition is 4  $\text{Hg}_2\text{O}$ , 3  $\text{NO}_5$ , 2 aq. Marignac finds that by boiling the mother liquors of the preceding salts, upon an excess of mercury for several hours, oblique colourless prisms are deposited, to which he assigns the formula, 5  $\text{Hg}_2\text{O}$ , 3  $\text{NO}_5$ , 2  $\text{HO}$ . Other subnitrates appear to exist.

A neutral *nitrate of the red oxide*, 2 ( $\text{HgO}$ ,  $\text{NO}_5$ ),  $\text{HO}$ , is slowly formed in voluminous crystals, by dissolving the red oxide of mercury in an excess of nitric acid, and evaporating the liquid until it assumes a syrupy consistence. Another nitrate, 2  $\text{HgO}$ ,  $\text{NO}_5$ ,  $\text{HO}$ , is deposited in acicular crystals from a boiling solution of mercury in excess of nitric acid; but it is obtained with greater certainty by saturating nitric acid, of sp. gr. 1.4, diluted with an equal bulk of water, with the red oxide of mercury. The solutions of both these salts are decomposed when diluted freely with water; a white insoluble basic nitrate, 3  $\text{HgO}$ ,  $\text{NO}_5$ ,  $\text{HO}$ , is precipitated: by long-continued washing with hot water, the whole of the nitric acid is removed from this basic salt, and oxide of mercury is left. Solutions of the nitrates of the red oxide of mercury, when digested upon an excess of the metal, are converted into nitrate of the suboxide.

(786) CHARACTERS OF THE SALTS OF MERCURY.—Most of the salts of mercury are colourless, but some of the basic salts of the red oxide are yellow. The following characters are common to the salts of both oxides. The soluble compounds have an acrid, nauseous, metallic taste: in large doses they act as irritant poisons. All the compounds of mercury are volatilized by heat. If a small quantity of any of the dry salts of this metal be placed at the bottom of a tube of the diameter of a quill, and be covered to the depth of an inch with a layer of dried carbonate of soda or potash, mercury may be obtained in the form of a sublimate of minute globules, by heating the upper part of the layer of the carbonate to redness, and slowly driving the vapour of the mercurial compound over it.

The presence of mercury, when in solution, may be detected by placing a small portion of the liquid on a piece of gold such as a half-sovereign, and touching the metal through the liquid with a scrap of zinc, or with the point of a steel knife. The mercury will

be deposited by voltaic action in the form of a white stain upon the gold. This stain will disappear on heating the gold to redness. The salts of mercury, whether soluble or insoluble, are all reduced to the metallic state when heated with a solution of *protochloride of tin*. A strip of metallic *copper* becomes amalgamated, if rubbed with a solution containing mercury.

1. *Salts of the suboxide of mercury* are characterized when in solution, by yielding with *caustic potash*, *soda*, or *lime*, a black precipitate of suboxide of mercury. *Ammonia* also gives a black precipitate. *Ferrocyanide of potassium* gives a white precipitate. *Sulphuretted hydrogen* and *hydrosulphate of ammonia* each yields a black sulphide of mercury. *Hydrochloric acid* and solutions of the *chlorides* cause a white precipitate of calomel, which is blackened by the addition of an excess of ammonia. *Iodide of potassium* gives a green subiodide of mercury; and *chromate of potash* a bright red subchromate of the metal.

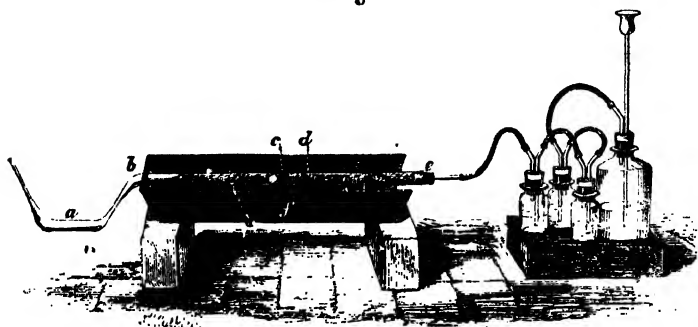
2. *Salts of the red oxide*, when in solution, yield with solutions of *potash*, *soda*, or *lime*, a bright yellow precipitate of oxide of mercury; with *ammonia*, a white precipitate; with *neutral carbonate of potash*, a yellow precipitate of oxide; with *bicarbonate of potash*, a red precipitate of oxychloride of mercury. *Hydrosulphate of ammonia* gives a black precipitate; and *sulphuretted hydrogen*, a dirty white precipitate, which passes through red into black. *Iodide of potassium* precipitates a salmon coloured iodide of mercury, which quickly becomes of a brilliant scarlet: this precipitate is soluble in excess both of iodide of potassium, and of bichloride of mercury. *Hydrochloric acid* and solutions of the *chlorides* give no precipitate with the salts of the red oxide of mercury.

(787) *Estimation of Mercury*.—Mercury is usually estimated in the metallic form. In the absence of lead and silver, it is often precipitated in this state from its solutions by means of *protochloride of tin*, acidulated with *hydrochloric acid*: the metal is collected on a weighed filter, and dried in vacuo over sulphuric acid.

When the compound is in the solid form, the plan recommended by Millon, for effecting the decomposition of the combinations of mercury and for collecting the metal is the following:—A hard glass tube, 15 or 16 inches long, such as is used in the analysis of organic compounds, is drawn out in the manner represented in fig. 312, and at *a* a small bulb is formed for the reception of the mercury; a plug of asbestos is placed at *b*; the tube is then filled as far as *c* with fragments of quick lime, and the mercurial compound in quantity varying from 15 to 50 grains is introduced between

*c* and *d*, and the tube is filled up with fragments of lime. If nitric acid be present in the compound, metallic copper must be substituted for quick lime. The extremity, *e*, is connected with an apparatus, *g*, which supplies a steady current of pure dry hydrogen; the tube being placed in a sheet-iron furnace, *f*; while the receiver, *a*, projects beyond

FIG. 312.



the furnace, and is kept cool. As soon as the apparatus is filled with gas, lighted charcoal is applied to the first third of the tube between *b* and *c*, and when it is at a full red heat, glowing charcoal is very gradually added until the whole length of the tube is red hot; the mercury collects in *a*, and the water, which is at first condensed, is gradually removed by the current of dry hydrogen. When the operation is over, the narrow portion of the tube between *a* and *b* is cut with a file, and the detached portion *a*, with its contents, is weighed; the mercury is emptied, the bulb cleaned with nitric acid and water, then dried, and weighed a second time; the difference gives the weight of the condensed mercury.

## § II. SILVER.

*Symbol*, Ag; *Equivalent*, 108; *Specific Gravity*, 10.53.

(788) SILVER has been known from the earliest ages, and has always been prized for its rarity, beauty, and its brilliant lustre. It has a white colour with a tinge of red; in hardness it is intermediate between copper and gold, and it is endowed with considerable tenacity; it may be hammered into very thin leaves, and admits of being drawn into very fine wire. By repeated heatings, however, this metal assumes a crystalline texture, and it then becomes extremely brittle. It crystallizes in forms belonging to the regular system. Silver fuses at  $1873^{\circ}$  F., and on cooling expands forcibly at the moment of solidification. It is not sensibly

volatile in closed vessels, but a silver wire is dispersed in greenish vapours when a very powerful electrical discharge is sent through it. It is, however, an excellent conductor both of heat and electricity, and is not inferior in these respects to any known substance. Silver is not oxidized by exposure at any temperature either to a dry or a moist atmosphere. Pure silver, however, when melted, absorbs oxygen mechanically, but the gas is given off at the moment of solidification: if a mass of melted silver be allowed to cool suddenly, the outer crust becomes solidified, and when the interior portion assumes the solid condition it ruptures the crust; small tubes or globules of melted metal are thus forcibly expelled by the escaping oxygen, aided by the sudden expansion which the silver undergoes in the act of solidification. This phenomenon, which is termed the *spitting* of the globule, is entirely prevented by the presence of 1 or 2 per cent. of copper. Silver has a powerful affinity for sulphur; by long exposure to the air the metal becomes superficially blackened or tarnished, from the formation of a thin film of sulphide upon its surface, owing to the decomposing action of the metal upon the small portion of sulphuretted hydrogen which is constantly floating in the air, especially of large towns.

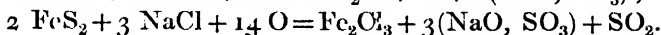
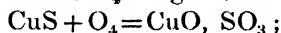
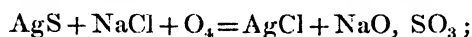
The best solvent for silver is nitric acid, which, if diluted with an equal bulk of water, acts upon the metal with great violence, dissolving it rapidly and evolving binoxide of nitrogen, while nitrate of silver is formed. Hydrochloric acid acts but slightly upon it. Aqua regia attacks it more rapidly. Boiling oil of vitriol oxidizes it with evolution of sulphurous acid. If common salt be moistened and left in contact with silver, it gradually corrodes it. The alkalis exert scarcely any action upon it, whether in solution or when fused by heat, and hence crucibles for the fusion of refractory minerals with caustic potash, are commonly made of this metal.

The value of silver as a medium of exchange has caused it to be adopted as such by all civilized nations from the earliest ages of the world. When alloyed with certain proportions of copper it is used for the current coin of the realm, and for the various articles of plate. From its superior power of reflecting light, it forms the best surface for the reflectors employed in lighthouses at sea.

(789) *Extraction of Silver from its Ores.*—Silver is frequently met with in the native state; either pure, when it occurs in filigree masses, or crystallized in cubes or octohedra, or sometimes combined with gold, mercury, or antimony: generally, however, it is found in combination with sulphur, mixed with sulphides of lead, antimony, copper, and iron. The mines of Peru and Mexico are the most extensive sources of silver. In Europe, those of Kongs-

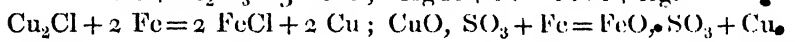
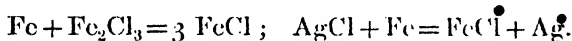
berg in Norway, and of Schneeberg and Freyberg in Saxony, are celebrated: there are also numerous other mines from which smaller quantities are obtained. The ores of silver occur usually among the primitive rocks, frequently in calcareous veins, traversing either gneiss, or slaty and micaceous deposits.

At Freyberg, silver is for the most part extracted from the sulphide by the method of *amalgamation*. The plumbiferous ores are in this case rejected, as they are not adapted to this method of proceeding, but are treated in the manner already mentioned, when speaking of the ores of lead (753). The ores are usually sorted, so that they shall contain about 0.24 parts of silver in 100, or about 80 ounces per ton of ore, and not more than 1 per cent. of copper; the proportion of iron pyrites is not allowed to exceed, or greatly to fall short of 35 per cent. The metalliferous mass, after being reduced to a coarse powder, is mixed with  $\frac{1}{10}$ th of its weight of common salt, and sifted, to ensure its intimate incorporation; it is then roasted, at first at a low red heat: during this operation, care is taken to keep the mixture constantly stirred, in order as far as possible to prevent it from concreting into lumps. Meantime arsenic and antimony are expelled in dense white fumes of arsenious acid and oxide of antimony, and the sulphides of the other metals are partially oxidized: the silver obtains chlorine from the salt, the sodium of which unites with oxygen and sulphur, chloride of silver and sulphate of soda being formed; the copper and the iron are changed, partly into sulphates, partly into chlorides, and partly into oxides, as the equations subjoined will show:—



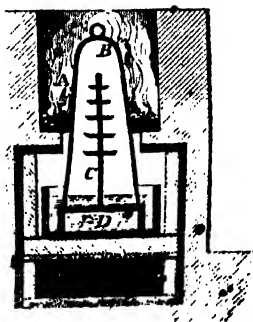
During the early stages of this operation, fumes of sulphurous acid are given off abundantly, and the roasting is continued until these are in great measure replaced by chlorine and perchloride of iron. A charge of  $4\frac{1}{2}$  cwt. requires 6 hours' roasting. The roasted mass is now raked out of the furnace, and is allowed to cool; it is next sifted in order to separate the lumps, which are powdered and are again submitted to the same operation. About 85 per cent. of the silver is thus converted into chloride at the first roasting. The portions which have passed through the sieve are ground to a fine powder, and passed through a bolting sieve to procure a meal of extreme fineness. This powder is next placed, with from a third to half its weight of water, in large casks, which are

charged with half a ton of the ore. These casks are caused to revolve upon horizontal axes, about 20 times per minute; 1 cwt. of scrap wrought-iron is then introduced into each cask, and after the lapse of an hour, 5 cwt. of mercury is added, after which the casks are again made to revolve for about 20 hours: during this operation a slight rise of temperature is observed. The mixture in the casks consists principally of chloride of silver mixed with large quantities of sulphate and dichloride of copper, and of the sesquichloride of iron, with a variable proportion of the oxides of the two latter metals. The object of agitating the mixture with the iron before adding the mercury, is to reduce the sesquichloride of iron to protochloride in the first instance; if this precaution were not taken, the mercury would be partially converted into calomel, which would not subsequently be decomposed, and would thus be lost: the excess of iron afterwards removes the chlorine from the chloride of silver, and dichloride of copper, and the sulphuric acid from the copper:—



The silver and copper thus set at liberty, immediately unite with the mercury, forming a liquid amalgam: the presence of the mercury favours this reaction, by establishing a voltaic current. At the expiration of 18 or 20 hours the casks are filled up with water, and are again set in motion for a couple of hours to allow the amalgam to be washed out of the spent materials; after which the fluid amalgam is drawn off into sacks of ticking; these sacks form a kind of rude filter through which the greater part of the mercury runs into a stone trough, leaving behind it a soft solid containing from 15 to 17 per cent. of silver. The mud in the casks is again submitted to washing; the residual amalgam subsides owing to its greater density, and the lighter portions are rejected. The filtered part of the mercury, which retains a small quantity of silver, is used again for the amalgamation of a fresh portion of ore. The silver in the solid amalgam has now to be separated from the remaining mercury; for this purpose it is placed in trays, supported on a tripod, c, fig. 313, under a large distillatory iron bell, B, round the upper part of which a fire, A, is lighted; the bell and its contents are thus brought to a red heat, by which means the mercury is driven off; its va-

FIG. 313.





pour descends, and is condensed in the water contained in the vessel, D. The operation is generally performed on 5 cwt. of amalgam at a time, and occupies 8 hours. The residual spongy mass of silver and copper is then fused and cast into ingots, which in the Saxon mines consist usually of about 70 parts of pure silver and 28 of copper per cent.\*

(790) *American Process of Amalgamation.*—In the mining districts of Mexico and Chili, where fuel is expensive, and where ores are often worked of a much poorer description than in Europe, the process of amalgamation is different. A good deal of the silver occurs in the native state, so that it unites directly with the mercury. The mineral is stamped and ground to a fine powder in mills, then moistened with water, and mingled with from 1 to 5 per cent. of salt; the mixing is effected by the trampling of horses during 6 or 8 hours. The ore thus blended with the salt is allowed to remain undisturbed for some days, after which an addition of  $\frac{1}{100}$ th or  $\frac{1}{200}$ th of its weight of what is technically termed *magistral*, is made. This substance consists of roasted copper pyrites, and contains about 10 per cent. of sulphate of copper, the remainder being sulphate of iron and other impurities; mercury, to the extent of twice the quantity of silver that the ore contains, is then added, the mixture being effected as before, by the trampling of horses. It is again allowed to rest for 16 or 20 days: during this period a considerable portion of the silver becomes united with the mercury, and

An improvement upon this process has been introduced by Augustin, who dispenses with the use of mercury altogether. After the ore has been roasted first by itself, and again a second time with chloride of sodium, it is digested in a concentrated solution of common salt;—such a solution dissolves chloride of silver readily: a dilute solution of chloride of sodium exerts little or no solvent action; and the concentrated liquid when diluted deposits the chloride of silver which it had previously dissolved. In practice it is found better, instead of diluting the liquid, to digest it upon metallic copper; the chloride of silver is decomposed, chloride of copper is formed and dissolved, whilst metallic silver is precipitated. The presence of chloride of copper in the solution of the chloride of sodium does not prevent the liquid from being employed again for the extraction of chloride of silver from fresh portions of the roasted ore.

Another important improvement in the operation was made by Ziervogel. He avoids the preparation of chloride of silver entirely, and merely roasts the sulphurous ores, in such a manner that the sulphates of iron and copper are completely decomposed, whilst the sulphate of silver, which withstands a much higher temperature, remains undecomposed in the mass. In this operation the powdered ore is roasted till it gives off no odour of sulphurous acid, and yields no sensible amount of sulphate of copper when thrown red-hot into water: boiling water then dissolves out the sulphate of silver, but the oxides of copper and iron remain undissolved. The silver is precipitated from the liquid by means of metallic copper as before. Both these processes have been patented and practised on a large scale in England.

at the same time a large quantity of calomel is formed. Another equal quantity of mercury is added, and a still longer interval of rest is allowed; then a third dose of mercury to the same extent follows; by this last addition a fluid amalgam is obtained, which is separated by washing, filtered, and the mercury is expelled from the silver by distillation. The quantity of mercury consumed in this process varies from 130 to 150 parts for each 100 parts of silver extracted, great waste being incurred owing to the formation of calomel, which is not recovered. It is calculated that up to the close of the last century, 6 million cwt. of mercury had thus been lost by the processes adopted in the American mines in the course of 200 years.

The theory of this operation is rather obscure. The sulphate of copper of the magistral, and the chloride of sodium decompose each other, chloride of copper and sulphate of soda being formed. Chloride of copper, in the presence of metallic silver, is converted into dichloride of copper, whilst chloride of silver is produced;  $2 \text{CuCl} + \text{Ag} = \text{Cu}_2\text{Cl} + \text{AgCl}$ . When dichloride of copper, with excess of common salt and water, is brought into contact with sulphide of silver the dichloride of copper is dissolved by the solution of chloride of sodium; the copper is converted into sulphide, whilst chloride of silver, is formed by double decomposition;  $\text{Cu}_2\text{Cl} + \text{AgS} = \text{Cu}_2\text{S} + \text{AgCl}$ . The excess of salt dissolves the chloride of silver, and the addition of mercury decomposes this dissolved chloride; calomel is formed, and an amalgam of silver is procured;  $\text{AgCl} + \text{Hg}_2 = \text{Hg}_2\text{Cl} + \text{Ag}$ . If too much magistral be added, an excess of chloride of copper,  $\text{CuCl}$ , is produced; this state of the mixture is easily perceived, as in such a case the globules of mercury in the mixture appear to be too minutely divided; the addition of lime then becomes necessary in order to decompose the excess of the chloride of copper, otherwise this salt would reconvert the silver into chloride, and the mercury into calomel.

(791) *Separation of Silver from Copper by Liquation.*—It occasionally happens that a copper ore contains a considerable amount of silver, which, under certain circumstances, it may be desirable to extract by the process of *liquation*. For this purpose, the copper having been brought to the stage of blister copper (733), is melted with from 3 to 4 times its weight of lead; the mixture is cast into circular ingots in iron moulds, which suddenly cool the alloy, and cause it to solidify before the copper and lead have time to separate. The proportion of lead should not be less than 500 times that of the silver in the mass. These cakes are

then subjected to the action of a moderate heat ; the lead, combined with nearly all the silver, and a small proportion of copper, gradually runs from the mass, leaving a spongy residue, consisting chiefly of copper, but still retaining a small proportion of lead. The argentiferous lead is then subjected to the process of cupellation (753), whilst the copper from which it has been separated is subjected to a patient roasting to oxidize the remainder of the lead, and is then refined much in the usual manner.

(792) *Plating and Silvering.*—Silver is frequently employed to give a coating to the surface of less expensive metals. Goods so prepared are said to be *plated* if the proportion of silver be considerable, and *silvered* if it be small. Plating on copper is effected by polishing the upper surface of the ingot which is to be plated, and then placing upon it a bright slip of silver, the superficial area of which is a little smaller than that of the copper which it is intended to cover. The thickness of the plate of silver in proportion to that of the copper varies with the value of the goods. The compound ingot is then exposed to a temperature just below the fusing point of the silver, which softens at its surface. By hammering or rolling out at this high heat, the two metals are *sweated* together, as it is termed, and become inseparably united. No solder is used in this process, but a small portion of powdered borax is placed round the edge of the silver to prevent the surface of the copper from becoming oxidated. The ingot is then rolled until it is reduced to the required degree of tenuity.

Plating on steel is effected rather differently. The article (a dessert knife, for example), having been first brought to the shape required, is tinned upon its surface, and then a slip of silver foil is soldered on. After the silver has been attached, the superfluous portion is removed, and the article is finished up and polished.

These methods of plating have, however, been in a great degree superseded by the process of electro-plating, in which the silver is deposited upon the surface by voltaic action. The mode of doing this will be explained hereafter.

Silvering may be effected either by the *wet*, or by the *dry* method. The wet method is usually adopted for such purposes as the silvering of thermometer scales. It is generally executed either on brass or copper : the surface of these metals is cleaned by *dipping*, or momentary immersion of the articles in nitric acid, to remove the film of oxide which always forms from exposure to the atmosphere, even for a few hours. They are then rubbed over with a mixture of 100 parts of cream of tartar, 10 of chloride of

silver, and 1 part of corrosive sublimate. The mercury appears to act as a kind of solder to the silver; the copper combines with the chlorine both of the chloride of silver and of the sublimate; the surface is afterwards polished.

Dry silvering is effected by dissolving a certain quantity of silver in mercury; the 'dipped' articles are agitated with a portion of this amalgam, which diffuses itself uniformly over the surface. By the application of heat the mercury is expelled, leaving a very thin film of silver behind: on polishing the trinkets a bright silvered surface is obtained.

(793) *Silvering of Mirrors*.—Some of the salts of silver when mixed with certain organic solutions are reduced to the metallic state, the silver being deposited upon the surfaces of glass vessels, in which the experiment is made, in the form of a brilliant, silvery, mirror-like coating. Mr. Drayton some years ago proposed to apply this observation to the silvering of mirrors upon the large scale, as the coating adapts itself not only to flat surfaces, but to those also which are curved, or cut into patterns. This process, according to MM. Pelouze and Fremy (*Traité de Chimie*, Second Edition, III., 347), is now successfully practised at Paris, as follows:—600 grains of pure neutral nitrate of silver are dissolved in 1200 grains of water. To this solution are added: 1st, 75 grains of a liquor prepared from 25 parts of distilled water, 10 of sesquicarbonate of ammonia, and 10 of solution of ammonia, of sp. gr. 0.980; 2nd, 30 grains of solution of ammonia, sp. gr. 0.980; and 3rd, 1800 grains of alcohol, sp. gr. 0.850. The mixture is left at rest to become clear. The liquid is decanted or filtered, and a mixture of equal parts of alcohol (sp. gr. 0.850) and of oil of cassia is added in the proportion of 1 part of this *essence of cassia* to 15 parts of the solution of silver; the mixture is agitated and left to settle for several hours, after which it is filtered. Just before pouring it upon the glass to be silvered, it is mixed with  $\frac{1}{8}$  of its bulk of *essence of cloves* (composed of 1 part of oil of cloves, and 3 of alcohol, sp. gr. 0.850). The glass having been thoroughly cleansed, is covered with the silvering liquid, and warmed to about  $100^{\circ}$  F., at which temperature it is maintained for 2 or 3 hours; the liquid is then decanted, and may be employed for silvering other glasses. The deposit of silver upon the glass is washed, dried, and then varnished.

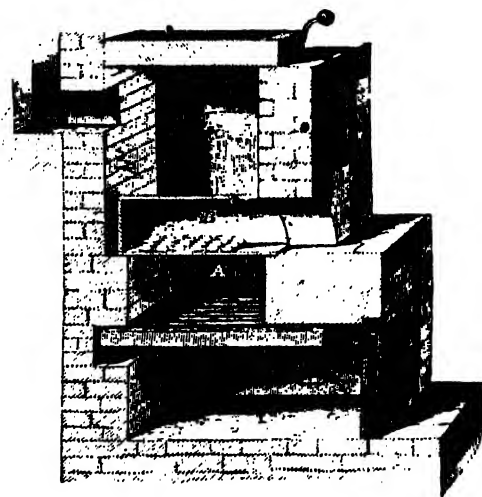
An alcoholic solution of grape sugar produces the same result, if substituted for the oils of cassia and cloves, but the deposit occurs much more slowly.

(794) *Alloys of Silver*.—Various alloys of silver may be obtained with facility, but the only one extensively used, except the amalgam for the purposes of silvering, is the alloy of silver with copper. Pure silver is too soft for ordinary uses, such as the fabrication of coin and jeweller's work, and would soon waste by the constant friction it would experience. In order to confer a sufficient degree of hardness upon the silver, it is combined with a small portion of copper. The proportion of copper in the 'standard' silver employed for coinage varies in different countries: in England it amounts to 7·5 per cent., in France to 10 per cent., and in Prussia to 25 per cent. Silver and copper in uniting to form an alloy expand slightly, so that the density of the mixture is somewhat less than the calculated mean. English standard silver has a density of 10·20, instead of 10·35. Experience has shown that an alloy of silver and copper, however carefully the two metals be incorporated, undergoes when melted a species of liquation as the mass slowly solidifies; when cast into ingots, the interior parts of the bars have a composition different from that of the superficial portions: a circumstance of some importance in the preparation of standard silver for the purposes of coinage. The only alloy in which this partial separation of the two metals was found not to occur is stated by M. Levol (*Ann. de Chimie*, III., xxxvi. 220), to consist of 719 parts of silver and 281 of copper, corresponding to the formula  $\text{Ag}_3\text{Cu}_1$ . This liquation is comparatively trifling in amount in bars which contain 950 parts of silver and upwards in 1000: in bars which contain a larger proportion of silver than 719 in 1000 of alloy, the central portions of the ingot were found to be richer than those upon the surface; but in alloys of lower value the proportion of silver was greatest on the surface of the ingot.

(795) *Assay of Silver by Cupellation*.—From the high price of silver compared with that of the metals used to harden it, it has become an object of great importance to be able to determine with facility and with accuracy, the proportion of silver in any compound. Jeweller's silver must according to law be of a certain degree of fineness. In this country each article, previous to being sold, is tested at Goldsmiths' Hall, and if approved is stamped. The method of testing commonly employed is termed *assaying* or *cupellation*. In principle it depends upon the property which lead possesses of absorbing oxygen at a high temperature, and of forming with it an easily fusible oxide, which imparts oxygen with facility to all metals, the oxides of which are not reducible by heat alone. The oxides thus formed unite with the oxide of lead, and produce a fusible glass, which is easily absorbed by a porous crucible made

of burnt bones, termed a *cupel*, whilst any silver that the mixture contains is left behind in a bright globule, which admits of being accurately weighed. The cupel and its contents are shown in section in fig. 314. The cupels are prepared from bone ash (burnt to whiteness, and ground to a fine powder), by moistening it with water; a suitable quantity of the mixture is placed in a mould, and the required form and coherence is given to it by the blow of a mallet or of a press: the cupels are allowed to dry thoroughly before they are used. The assay may be conducted upon quantities of silver varying from 10 to 20 grains in weight. The plan of proceeding is as follows:—In a convenient furnace, such as is shown in section at A A, fig. 315, is placed an earthenware oven or muffle, B, of semicylindrical form, closed at one end, and open at the other, with slits in the sides to allow the free circulation of the air; upon the floor of the muffle, a number of cupels are arranged in rows, and the temperature is raised to bright redness. Equal portions of the various samples of silver to be assayed, are in the meantime accurately weighed, and wrapped in a quantity of pure thin sheet-lead, the weight of which varies with the purity of the alloy; the larger the proportion of foreign metals that it contains, the greater is the quantity of lead needed. Each piece for assay is now placed in its allotted cupel, by means of a long pair of tongs. It quickly fuses; fumes of oxide of lead are seen rising from the cupels, but the greater part of the oxide is absorbed by the cupel, and the silver is left behind in a state of purity. At the moment that the last portion of lead undergoes oxidation, the surface of the silver flashes, or lightens, as it is technically termed, owing to the cause already explained (753). This phenomenon indicates that the process is completed. The button is allowed to cool very gradually, to prevent the loss of silver by

FIG. 315.



dispersion from *spitting* (788); it is then detached from the cupel, brushed, and accurately weighed. If the piece of alloy originally taken weighed 10 grains, the weight of the button in hundredths of a grain gives the number of parts of silver in 1000 parts of alloy. A minute quantity of silver always passes into the cupel during the process, for which an allowance must be made in weighing the button; and if the proportion of lead be too great this loss is increased, but if too little be used, part of the copper is left in the bead. Upon an alloy which contains 925 parts of silver to 75 of copper, the loss is about 4 per 1000; and upon silver which contains 900 parts in 1000, the loss on the button is about 5 parts in 1000. In order to be able to estimate the amount of this loss in each operation, the best plan is to pass three or four *proofs*, with each set of assays. These proofs consist of pieces of fine silver of known weight, which are mixed with quantities of lead and copper, approximatively of the same amount as those present in the assays under trial. The loss experienced by these proofs affords a method of checking the results of the assay.

The most convenient system of reporting the fineness of silver, is the decimal method, which is employed in most countries with the exception of England. The practice has lately been introduced by Sir J. Herschel into the Mint of this country, and it probably will gradually supersede the cumbrous and artificial method which is still generally employed by the English assayers. Upon the decimal system fine silver is termed 1000·0, and the report upon any sample of alloy simply indicates the number of parts of pure silver in 1000 which it contains. Thus, English standard silver contains 925 parts of silver, and 75 of copper in 1000 of alloy. French standard contains 900 parts of silver, and 100 of copper in 1000 of alloy. English standard would therefore be reported as 925; French standard as 900.

The proportions of lead which are generally employed for the cupellation of different alloys are the following:—

If 1000 parts of the alloy contain	It will require of lead
1000 parts of fine silver . . .	half its weight.
950           "           . . .	3 times its weight.
925           "           . . .	5½       "
900           "           . . .	7       "
850           "           . . .	9       "
800           "           . . .	10       "
700           "           . . .	12       "
600           "           . . .	14       "
500, or less,,           . . .	16 or 17,,

A skilful assayer will generally be able at once to determine the comparative fineness of an article from its mere appearance, and will judge accordingly of the proportion of lead which it will require. Great care is needful in regulating the temperature of the furnace during the cupellation: if too high, a part of the silver will be lost by volatilization; if too low, portions of lead and copper are liable to be retained. When the assay is properly performed, the button is brilliant, well rounded, free from irregularities and somewhat granular upon its surface: it is readily detached from the cupel. If the assay adheres strongly to the cupel, or is irregular in its outline, it retains a portion of alloy.

(796) *Assay of Silver by the Humid Process.*—The results of the process of the assay by cupellation, even in experienced hands, may vary as much as 2 parts in 1000: this circumstance induced Gay Lussac to contrive a different method, which is now adopted not only in the French Mint, but is employed in the Mints of Great Britain and the United States, as well as in almost all the Mints of Europe; it admits of an accurate estimate of the value of an alloy to within 0.5 in 1000. This process depends upon the precipitation of the silver in the form of an insoluble chloride, and the measurement of the amount of a standard solution of chloride of sodium which is required to effect the complete precipitation of the silver in a given weight of the alloy. Chloride of silver easily collects into dense flocculi by agitation in a solution which is acidulated with nitric acid, and which contains no excess of soluble chlorides; so that the exact point at which the precipitate ceases to be formed is readily perceived.

A solution of common salt is prepared of such a strength, that 1000 grains of it are exactly sufficient to precipitate 10 grains of pure silver. 10 grains of the alloy for examination are placed in a stoppered bottle, capable of holding about 6 oz. of water, and by the aid of a gentle heat are dissolved in 2 drachms of nitric acid, of specific gravity 1.25: the solution of salt is then placed in a burette (fig. 316) capable of holding rather more than 1000 grains. The burette, when filled with the solution, is weighed before being used, and the liquid is added to the nitrate of silver in the bottle, when it is supposed that the silver is nearly all precipitated, the liquor is briskly agitated in the bottle, and the precipitate is allowed to subside; a drop or two more of the solution of salt is then added: if a precipitate be produced, the liquid is again agitated; and when

FIG. 316.



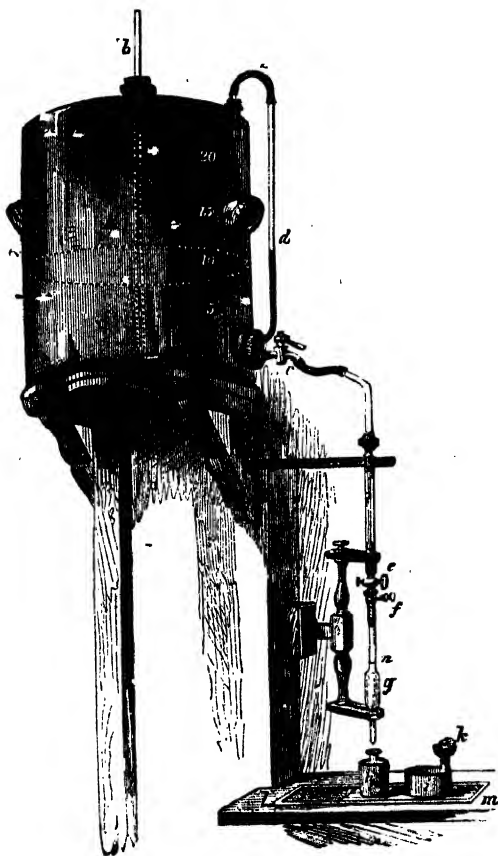


clear, more of the solution is added, as before, as long as any turbidity is produced by the addition. When a cloud ceases to be formed, the proportion of solution of salt which has been added, is ascertained by weighing the burette a second time. The number of grains of the solution employed indicates the degree of fineness of the alloy.

When, as in the assay of bars for coin, or for jeweller's work, a large number of assays have to be executed, all very nearly of uni-

form fineness, the operation may be reduced to a system by which its precision may be increased, at the same time that it is rendered much more easy of execution. For this purpose, two solutions of salt are employed: one, the *standard solution*, containing in 1000 grains a sufficient quantity of commercial chloride of sodium to precipitate 10 grains of silver;\* the second solution, the *decimal solution*, having one-tenth of the strength of the first, and being prepared by diluting 1 pint of the standard solution with 9 pints of water. These solutions are to be preserved in well closed bottles. The standard solution is prepared in large quan-

FIG. 317.

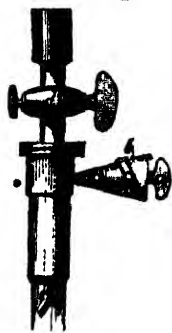


\* This solution contains approximately 380 grains of chloride of sodium in a gallon: but as the commercial salt contains chloride of magnesium, the exact strength must be determined by dissolving 10 grains of fine silver in acid, and precipitating it by the addition of 1000 grains of the solution, ascertaining the amount of the excess or deficiency of chloride in the manner about to be detailed, and then adding water or salt as may be needed.

titles at a time, and kept in stoneware jars, *A*, fig. 317, capable of containing 20 or 25 gallons; *b* is a small tube, which passes nearly to the bottom of the jar, to admit air, whilst the liquid is drawn off by the stop-cock, *c*, without allowing any loss by evaporation; *d* is a gauge by which the quantity of liquid within is indicated. A series of bottles fitted with ground stoppers, and capable of containing about 6 fluid ounces each, are numbered consecutively from 1 upwards; into each bottle 10 grains of the alloy for assay is weighed, 2 drachms of nitric acid are added to each bottle, which is placed in a shallow vessel containing water, and gradually raised to the boiling point; in ten minutes the alloy is completely dissolved.

The precipitation of the silver in the form of chloride is then effected by the aid of the apparatus now to be described:—*g*, fig. 317, is a glass pipette which can be filled with the standard solution, of known temperature, as indicated by the thermometer, *t*. The quantity of liquid introduced into the pipette is regulated by means of the stop-cock, *e f*, the peculiar construction of which is shown on a larger scale in fig. 318, in which *d*

FIG. 318.

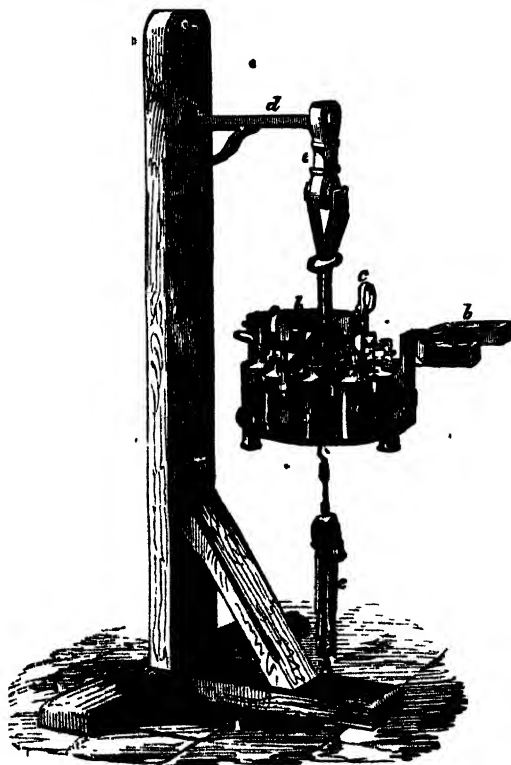


represents an ordinary stop-cock (constructed of silver to resist the action of the solution), terminating below in a long tube, *c*; at *b* is an opening for the escape of air, which can be closed at pleasure by the plug, *a*. Suppose it be desired to fill the pipette, *g*, fig. 317; the lower opening of the pipette is closed by the fore-finger, the solution is admitted by opening the stop-cock, *e*, whilst the air escapes at *f*, which is open; as soon as the liquid has risen a little above the mark, *n*, both the stop-cock, *e*, and the plug at *f* are closed, and the finger is withdrawn. In this position the pipette will retain its charge for an indefinite time. The apparatus represented at *ml* is intended to facilitate the exact emptying of the pipette; the tray, *h i*, slides easily between two grooves, in which its motion is limited by the stops, *l* and *m*; *h* is a compartment for the reception of the assay bottles, so adjusted that when the tray rests against the stop, *m*, the pipette shall empty itself into the bottle without wetting its neck; *i* is another compartment for receiving the superfluous solution of salt, and *k* represents a piece of sponge, the object of which is to remove the drop which hangs to the lower end of the pipette; the stop, *l*, is so placed, that when the slide rests against it, the sponge just touches the lower extremity of the pipette. The sponge, *k*, having been

brought to touch the lower end of the pipette, the plug at *f* is slightly relaxed to allow the air to enter, and a portion of the liquid gradually to escape, until it has fallen exactly to the mark, *n*. The slide is now moved until the bottle, *h*, is directly underneath the pipette, and on opening the plug at *f* to its full extent, the charge flows freely into the bottle.

Suppose now the object of the assay be to ascertain whether a certain number of bars be of the fineness of English standard silver, or if not, what is the amount of their variation from standard. The pipette, *g*, is so graduated that when filled up to the mark, *n*, it shall deliver exactly 9.22 grains of the standard solution, which will contain a sufficient amount of common salt to precipitate 9.22 grains of silver; a quantity which is purposely rather less than the assay is expected to contain; 10 grains of alloy, if of correct composition, containing 9.25 grains of silver. When

FIG. 319.



each bottle in succession has received from the pipette a charge of exactly the same value, the bottles are transferred to the *agitator* shown at fig. 319, which is suspended from an iron arm, *d*, between two strong springs, *e e*, made of vulcanized caoutchouc. This agitator is usually made to contain 10 bottles, which are lodged in the compartments, *a a*; the stoppers are secured in their places by the rims, *b b*, one of which is represented in the figure as thrown back for the admission of the bottles; the rims when closed are confined by the springs

shown at *c c*. On agitating the apparatus briskly for 60 or 80

seconds the solutions become clear, and the bottles are removed from the agitator, and transferred to a stand, behind which is a black board divided into 10 numbered compartments, each bottle being placed opposite the compartment which corresponds with its number.

The adjustment of the remaining portion of the assay is made by means of the *decimal solution*. This is contained in a small bottle of 10 or 12 ounces in capacity, fig. 320, provided with a tube or small pipette, *b*, open at both ends, but drawn out to a narrow aperture below. On this small pipette a mark, *c*, is made at a height corresponding exactly to 10 grains of the liquid; 10 grains of this solution containing sufficient chlorine to precipitate 0.01 grain of silver.

FIG. 320.



The assayer now plunges this small pipette into the decimal solution, and closing the upper opening of the tube with his forefinger, partially withdraws it from the bottle and allows the liquid to escape until it stands exactly at the line of the graduation, *c*; he then transfers the pipette to the first bottle, and allows the solution to flow into it. The same operation is repeated with each assay bottle in succession. A mark is then made with a piece of chalk, opposite to each bottle in which a precipitate is occasioned. These bottles are again replaced in the agitator, and shaken a second time; the solutions having thus again been rendered clear, are replaced upon the table, and a second pipette of the decimal solution is added to each of the bottles in which a precipitate was first produced. This operation is repeated until in each bottle no further precipitate is occasioned. The contents of the pipette, *g*, of the standard solution, which have been added to each assay, occasion a precipitate out of the 10 grains equal to 9.22, or of 922 parts out of 1000 parts of alloy. Each pipette of decimal solution is equivalent to  $\frac{1}{1000}$ th of fine silver in the alloy, and by counting the number of marks against each bottle, reckoning the last only as equal to  $\frac{1}{2}$ , since a portion of it probably remains in the liquid in excess, the assayer ascertains the value of each bar. If, for instance, two marks stand opposite to any bottle, the fineness of the bar will be more than 923, but less than 924, and may be reported as 923.5.

If, however, there be any bottles in which the addition of the first pipette of the decimal solution produces no precipitate, these

samples must be either exactly of the fineness 922, or below that point. The following method is adopted for completing the assay of these samples: a *decimal solution of silver* is prepared by dissolving 10 grains of pure silver in nitric acid, and diluting it with distilled water till the solution occupies the bulk of 10,000 grain measures of water, each 10 grains of this liquid will then contain exactly 0.01 grain of silver. A bottle of this solution is provided with a pipette similar to that shown in fig. 320, but graduated to deliver 50 grains of the liquid from the mark, *d*. Each of the assay bottles which indicates a fineness below 922, is supplied with 50 grains of this decimal silver solution, or with 0.05 grain of silver; a mark of —5 is made upon the board against each of these bottles. The bottles are then agitated as before, and a fresh dose of 10 grains of the decimal *salt* solution is now added to each; if a cloud be thus produced, a mark is chalked against each bottle in which a precipitate is observed, and the bottles are again agitated, and another dose of decimal salt liquid is added, and so on, until a precipitate ceases to form. Suppose that the first two pipettes of the solution produce a cloud, but the third does not; each bottle, it will be remembered, received a dose of salt solution in the first instance, as usual, in addition to the quantity received after the decimal silver solution was added; the quantity of salt which has produced a precipitate is therefore equivalent to  $922 + 1 + 1\frac{1}{2}$  or 924.5, but since 5 of silver have also been added beyond that which the alloy originally contained, the amount to be reported becomes 924.5—5, or the fineness of the bar is 919.5. It is preferable in cases where the bars are below the standard, to add an excess of silver at once, and then to estimate the excess of silver in the manner above described; because, if instead of acting thus, successive doses of 0.01 of silver be added until no further precipitate is formed, it becomes very difficult to render the solution clear by agitation.

The standard solution is prepared at a temperature, say of 60° F., consequently the pipette, *g*, will only deliver a volume of liquid rigorously equal to 9.22 grains of silver, at that temperature. At a higher temperature the liquid will expand, and a given volume will therefore contain a smaller amount of chloride of sodium, whilst at a lower temperature it will contract, and will contain a larger amount. A correction for this variation in the strength of the liquid is therefore required. This is made very simply in the following manner. Each time that a number of assays is made, a piece of fine silver, equal to 9.25 grains, is weighed off, dissolved in nitric acid, and assayed as above directed.

The number of pipettes of the decimal solution of salt which is required to complete the precipitation is noted, and the value of the contents of the large pipette, *g*, is thus verified upon each occasion. If, for example, 2½ pipettes were required for completing this precipitation, the large pipette would deliver a quantity of the solution sufficient to precipitate 9.225 grains on that day, instead of 9.22. Any deviation from the calculated value is allowed for, and a correction is made upon the assays by means of a table constructed for the purpose.

It is easy to apply this apparatus to the assay of silver of other degrees of fineness; but it is necessary to know approximatively the value of the assay, in order that a suitable weight of the alloy be dissolved in nitric acid. Suppose, for instance, a number of bars approximatively of the value of 900 (the French standard), are to be assayed; a piece of the assay, which contains approximatively 9.25 grains of fine silver, must be taken; the quantity required is easily calculated, since the weight of the alloy needed will be inversely as its fineness; for  $900 : 925 :: 10 \text{ grs.} : 10.277 \text{ grs.}$  The weight required in this case will consequently be 10.277 grains.

Mercury is the only metal the presence of which interferes with the accuracy of the assay by the humid method; but the process may be modified so as to give correct results even in this case.

(797) *Preparation of Fine Silver.*—In order that the foregoing process shall be accurately performed, it is necessary to be provided with silver of absolute purity. The following is the best method of procuring the metal in this condition. Standard silver is dissolved in nitric acid; the liquid is diluted and decanted or filtered from undissolved particles of gold or sulphide of silver, and the solution is precipitated by the addition of a solution of chloride of sodium in slight excess. The precipitate is washed in a large jar by subsidence, until the washings are tasteless. The chloride is then mixed with oil of vitriol, in the proportion of 3 ounces to each pound of chloride, and several bars of zinc are placed in the mass; the zinc speedily becomes converted into chloride of zinc, which is dissolved, whilst the silver is reduced to the metallic state, and by a voltaic action the reduction gradually extends through the mass;  $\text{Zn} + \text{AgCl} = \text{Ag} + \text{ZnCl}$ . The mixture is not to be agitated. In about a week's time the decomposition is usually completed. If a portion of the reduced silver, after being thoroughly washed, is entirely soluble in nitric acid, the reduction is complete. The bars of zinc, with the crust which adheres to them, are then carefully removed, and the reduced metal is digested for two days, with

dilute sulphuric acid, to remove any portions of zinc, and washed in a large vessel by subsidence, until the washings cease to precipitate nitrate of silver.\* The reduced silver is now redissolved in nitric acid, and a second time precipitated as chloride; pure hydrochloric acid being employed for this purpose; the precipitated chloride is again washed by subsidence until the washings no longer reddened litmus. The chloride of silver is next dried until it ceases to lose weight, 100 parts of the chloride are mixed with 70.4 of chalk, and 4.2 of powdered charcoal, and the mixture is heated in a deep clay crucible. The temperature is kept at a dull red heat for half an hour, after which it is gradually raised to full redness: a considerable disengagement of gas takes place, owing to the evolution of carbonic acid and carbonic oxide, and oxychloride of calcium is formed, constituting a fusible slag, beneath which the pure silver collects;  $\text{AgCl} + 2(\text{CaO}, \text{CO}_2) + \text{C} = \text{CO} + 2 \text{CO}_2 + \text{CaO}, \text{CaCl} + \text{Ag}$ . The silver may be poured into an ingot mould, and afterwards rolled into sheets.

(798) *Oxides of Silver*.—Silver forms three oxides; a sub-oxide,  $\text{Ag}_2\text{O}$ ; a protoxide,  $\text{AgO}$ , which is the basis of the salts of the metal; and a peroxide,  $\text{AgO}_2$ , which does not combine with acids.

*Protoxide of Silver, (AgO), Eq. 116*.—This oxide may be procured by adding a solution of potash or of soda to a solution of the nitrate or any soluble salt of silver. A brown hydrated oxide falls, which readily parts with its water, and if dried at a temperature above  $140^\circ$ , becomes anhydrous; it gives off oxygen below a red heat, and becomes reduced to the metallic state. Oxide of silver is a powerful base; it combines easily with acids, and forms with nitric acid a salt which is neutral in its reaction upon litmus. It is slightly soluble in water, to which it communicates a feeble alkaline reaction. Potash and soda do not dissolve it, but it is freely soluble in ammonia, and the solution, by exposure to the air, deposits a black micaceous powder, which is powerfully explosive, and which has received the name of fulminating silver.

(799) *Fulminating Silver* is also produced if concentrated ammonia be digested for some hours upon freshly precipitated oxide of silver; a black powder is formed which is allowed to dry in minute quantities on separate pieces of filtering paper. The same compound is formed on precipitating an ammoniacal solution

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\* The reduced silver may be dried, and cast into ingots if desired. The metal is refined in large quantities for commercial purposes in this manner. It is not absolutely pure, and therefore, for delicate chemical operations, it undergoes the further process of purification described in the text.

of nitrate of silver by the addition of potash. It is necessary to be aware of these facts, as it is a most dangerous substance, and might easily be produced unintentionally. Friction or pressure, even when under water, occasions it to explode: and when dry, its detonation often occurs without any assignable cause. Acids immediately decompose it into an ammoniacal salt, and the corresponding salt of silver. The composition of this body, owing to its dangerous character, has not been accurately determined, but it is generally supposed to be a nitride, similar to that which is obtainable from mercury.

*Suboxide of Silver* ( $\text{Ag}_2\text{O}$ ).—If the citrate of silver be heated to  $212^\circ$  in a current of hydrogen, the salt loses half an equivalent of oxygen, and a compound is produced which is sparingly soluble in water, forming with it a brown solution, from which, on the addition of potash, a suboxide of silver is precipitated. This compound is very unstable; it is decomposed by acids and by ammonia into protoxide of silver and metallic silver.

*Peroxide of Silver*, ( $\text{AgO}_2$ ), *Eq.* 124; *Sp. Gr.* 5.474.—This compound is procured in dark grey acicular crystals when a dilute solution of nitrate of silver is decomposed by means of the voltaic current. The peroxide of silver accumulates upon the positive plate, but it always retains a certain quantity of undecomposed nitrate of silver. It is a conductor of the voltaic current. Acids decompose it, forming a salt of the protoxide, whilst oxygen gas escapes. It is also decomposed by ammonia, with effervescence, owing to escape of nitrogen.

•(800) *Sulphide of Silver*, ( $\text{AgS}$ ), *Eq.* 124; *Sp. Gr.* 7.2.—This compound is the principal ore of silver. It is found native, sometimes crystallized in cubes or octohedra; at other times massive. It has a leaden-grey metallic lustre, from which it derives its mineralogical name of *silver glance*. ~~Sulphide of silver~~ is isomorphous with subsulphide of copper, and sometimes displaces it in certain minerals, such, for example, as polybasite, and fahlerz or grey copper.

Silver has a very powerful affinity for sulphur. The metal becomes tarnished owing to the formation of a film of sulphide if it be exposed to the action of sulphuretted hydrogen in the gaseous state, even though largely diluted with air; and a black spot is immediately produced upon its surface by contact with a solution of an alkaline sulphide. Sulphide of silver may be prepared by transmitting a current of sulphuretted hydrogen through solutions of the salts of silver, in which it forms a black precipitate; or it may be obtained by heating silver with an excess of sulphur in a



covered crucible. The sulphide of silver fuses, and forms a dark grey crystalline mass as it cools, and the excess of sulphur is volatilized.

Sulphide of silver is soft enough to allow of its being cut with a knife; it also possesses sufficient malleability to receive impressions from a die. It is not a conductor of the voltaic current when cold, but if heated it readily transmits the current without undergoing decomposition. It is easily fusible, and if heated in close vessels may be melted without becoming decomposed; but if roasted in the air, the sulphur is gradually converted into sulphurous acid, and metallic silver is left: during this operation a part of it is usually converted into sulphate of silver, which afterwards requires an elevated temperature for its decomposition.

Sulphide of silver is decomposed when boiled with concentrated sulphuric acid, sulphurous acid and sulphate of silver being formed. Boiling hydrochloric acid converts it into chloride of silver, with evolution of sulphuretted hydrogen. Chloride of copper converts it into chloride of silver, with the formation of subchloride of copper and sulphide of copper. This change is much facilitated by the presence of chloride of sodium in a moist state, as both the chloride of silver and the subchloride of copper are dissolved at the moment of their formation. These reactions become important in the extraction of silver from its ores (790). Sulphide of silver is also decomposed when heated with the alkalis, and a similar effect is produced by ignition with iron, copper, lead, and many other metals.

Sulphide of silver may be made to unite with many other metallic sulphides when fused with them. A native compound of this description is found in *red silver ore*, which is a double sulphide of silver and antimony,  $3\text{AgS}, \text{SbS}_3$ . In this mineral a portion of sulphide of antimony is often displaced by sulphide of arsenic.

(801) *Chloride of Silver*, ( $\text{AgCl}$ ), *Eq.* 143.5; *Sp. Gr.* 5.552.—This compound is found native, either crystallized in cubes, or as a compact semi-transparent mass, known by the name of *horn silver*. It is procured as a dense white flocculent precipitate by adding hydrochloric acid or the solution of any chloride to a soluble salt of silver; when moist, it quickly assumes a violet-colour by exposure to the sun's light; a similar change is produced gradually by diffused daylight. A dark oxychloride appears to be formed under these circumstances, and hydrochloric acid is set free.

Chloride of silver is insoluble in pure water, and in all the

**diluted acids.** It is taken up by boiling hydrochloric acid and by strong solutions of the chlorides of metals of the alkalis and alkaline earths, with which it forms crystallizable double salts; they are decomposed if their solutions are diluted; advantage is taken of this circumstance in the extraction of silver. (Note, p. 1028.)

Chloride of silver melts at a temperature of about  $500^{\circ}$ , and is partially volatilized; on cooling it forms a horny semi-transparent sectile mass. It is not decomposed when heated with carbon; but is easily reduced by hydrogen, if it be heated in a current of the gas, hydrochloric acid and metallic silver being formed: zinc, and iron, and many of the easily oxidizable metals also reduce moist chloride of silver. On the large scale this process is turned to account in the refining of silver (797). It is not necessary that the chloride of silver be freshly precipitated, though if it be, the operation is more rapid: if a cake of the fused chloride be laid upon zinc or iron and covered with acidulated water, it will after some days be completely reduced to a spongy mass of metallic silver.

Weak alkaline leys do not act upon chloride of silver, but if a concentrated solution of potash be boiled upon it, chloride of potassium is formed, and a dense black oxide of silver is produced; the addition of sugar to this mixture reduces the oxide rapidly to the state of metallic silver. Ammonia dissolves the chloride freely, and deposits it again by evaporation in the cold, in transparent colourless crystals; if boiled, fulminating silver is deposited. When ignited with the alkaline carbonates, chlorides of their bases are formed and pure silver is left: this reaction furnishes a means of procuring large quantities of silver in a state of purity;  $\text{AgCl} + \text{NaO}, \text{CO}_2 = \text{NaCl} + \text{CO}_2 + \text{O} + \text{Ag}$ . Chloride of silver is soluble in solutions of the hyposulphites, forming compounds of an intensely sweet taste: by evaporation crystalline double hyposulphites may be procured (348). Cyanide of potassium likewise dissolves chloride of silver, forming chloride of potassium and a double cyanide of silver and potassium. The soluble sulphites also dissolve chloride of silver.

*Subchloride of Silver*, ( $\text{Ag}_2\text{Cl}$ ), may be obtained by digesting leaves of pure silver in chloride of copper or perchloride of iron; it forms black scales which are not acted upon by nitric acid, but are resolved by ammonia into the chloride and metallic silver.

(8q2) *Iodide of Silver*, ( $\text{AgI}$ , Eq. 235), is found in Mexico, mixed with carbonate of lime, native silver, and sulphide of lead. It may be procured artificially by precipitating the nitrate by iodide of potas-

sium, when a pale yellow flocculent deposit occurs. It is but slowly acted on by light, is insoluble in acids, and almost so in ammonia. It fuses easily, into a mass which becomes yellow and opaque on cooling. It is decomposed by zinc in the presence of moisture. Chlorine displaces the iodine from the salt. Iodide of silver is soluble in concentrated solutions of iodide of potassium.

The *Bromide of Silver*, ( $\text{AgBr}$ , *Eq.* 188), is of a yellowish colour, is insoluble in water, and is much less soluble in ammonia than the chloride. Acids do not dissolve it, but chlorine disengages vapours of bromine from it, and chloride of silver is produced. Bromide of silver is formed by the addition of solution of bromide of potassium to a solution of nitrate of silver. The precipitate is soluble in a concentrated solution of bromide of potassium and in other bromides, with which it forms double salts, which are decomposed by dilution with water. Both the bromide and the iodide of silver are soluble in a solution of hyposulphite of soda.

(803) *Sulphate of Silver*, ( $\text{AgO}$ ,  $\text{SO}_3$ ), *Eq.* 156; *Sp. Gr.* 5.322. — When silver is boiled with sulphuric acid, a portion of the acid is decomposed and gives oxygen to the silver which is converted into a sulphate, while sulphurous acid escapes: the sulphate is dissolved by the excess of acid, but is deposited in great part on the addition of water, of which it requires 90 times its weight for solution. It may be obtained in small rhombic prisms, which fuse readily; for their decomposition they require a temperature higher than is needed to decompose the sulphates of iron or copper. (See note, page 1028.) Small quantities of gold are separated from silver on the large scale, by boiling 1 part of the alloy finely granulated, in cast-iron vessels with  $2\frac{1}{2}$  parts of oil of vitriol; the gold is left behind as a fine powder: the solution of silver is afterwards diluted till of a specific gravity of 1.200, introduced into leaden vessels, and the silver precipitated in the metallic form from the solution by bars of metallic copper. Crystallized sulphate of silver absorbs 1 equivalent of ammonia with rapidity. A hot solution of ammonia dissolves the salt freely, and on cooling deposits crystals composed of ( $\text{AgO}$ ,  $\text{SO}_3 + 2 \text{H}_3\text{N}$ ).

(804) *Nitrate of Silver*, ( $\text{AgO}$ ,  $\text{NO}_3$ ) *Eq.* 170; *Sp. Gr.* 4.336. — This salt is readily formed by dissolving silver in moderately strong nitric acid. If standard silver be employed in its preparation, the oxide of copper is easily separated from the solution by boiling it upon freshly precipitated oxide of silver, which may be prepared by precipitating a portion of the same solution by potash and washing the precipitate, the presence of oxide of copper being unimportant. It crystallizes in square, colourless,

anhydrous tables, which require an equal weight of cold water for solution. Boiling alcohol also dissolves about a fourth of its weight of the salt, but deposits most of it on cooling. The nitrate fuses when heated, and if then cast into cylindrical moulds, it forms the sticks of *lunar caustic* employed by surgeons as an escharotic. By a more elevated temperature it is decomposed, and metallic silver is left.

Nitrate of silver, when pure, undergoes no change by the action of light; but it is readily decomposed by the combined action of light and organic matter, which it usually stains black. The stain thus produced cannot be removed by washing with soap and water; from this property it has been employed as the basis of an ink for marking linen. Mr. Brande gives the following as a good formula for the preparation of marking ink:—Dissolve 2 drachms of nitrate of silver and 1 drachm of gum arabic in 7 drachms of water, and colour the liquid with Indian ink. It is requisite to prepare the cloth first, by moistening the spot to be marked with a solution of carbonate of soda, which is allowed to become dry. This preparatory solution may consist of 2 ounces of crystallized carbonate of soda, and 2 drachms of gum, dissolved in 4 ounces of water.

The black stains of nitrate of silver may be removed from the hands or from linen by the employment of a strong solution of iodide of potassium, or more easily by cyanide of potassium.

When metallic silver in fine powder is digested in a solution of nitrate of silver, it is dissolved, and a yellow solution is formed analogous to that obtained when lead is similarly treated (766).

(805) *Triphosphate of Silver*, ( $3 \text{ AgO}, \text{PO}_5$ ; *Eq.* 420; *Sp. Gr.* 7.321), is of a yellow colour, which is speedily changed by the action of light. The salt is very soluble in excess both of nitric acid and of ammonia. It is easily procured by precipitating a solution of the ordinary phosphate of soda by one of nitrate of silver; it fuses if heated above redness. The *pyrophosphate* ( $2 \text{ AgO}, \text{PO}_5$ ) is obtained in like manner by precipitating the nitrate of silver by pyrophosphate of soda; it is a white precipitate, slowly changed by light, and is easily fusible. The *metaphosphate* ( $\text{AgO}, \text{PO}_5$ ) is also obtained by precipitation from the nitrate of silver by the metaphosphate of soda; it forms a gelatinous mass which softens even at a heat of  $212^\circ$ , and is soluble in excess of nitrate of silver. If boiling water be poured upon this precipitate, it fuses; acid is removed, and a submetaphosphate is left, consisting of  $3 \text{ AgO}, 2 \text{ PO}_5$  (Graham).

(806) **CHARACTERS OF THE SALTS OF SILVER.**—The soluble

salts of this metal are colourless, and nearly all are anhydrous; they have a powerfully acrid, metallic, astringent taste, and act as irritant poisons. *Before the blowpipe* they are all readily reduced on charcoal to the metallic state, especially when mixed with carbonate of soda. Silver is used to impart a yellow colour to glass. In solution the salts of silver present the following reactions:—

The *fixed alkalies* give a brown hydrated oxide, insoluble in excess of the precipitant. *Ammonia*, a brown precipitate, readily soluble in excess of ammonia. *Carbonates of potash and soda*, a white carbonate of silver insoluble in excess, but soluble in carbonate of ammonia. *Sulphuretted hydrogen* and *hydrosulphate of ammonia* give a black precipitate of sulphide of silver, not soluble in ammonia, or in the alkaline sulphides. But the most characteristic test is the action of *hydrochloric acid* or a *soluble chloride*, which produces a white curdy precipitate of chloride of silver, which is insoluble in nitric acid, but readily soluble in ammonia; it is also soluble in hyposulphite of soda, with which it forms an intensely sweet solution: chloride of silver speedily assumes a violet tinge when exposed to light; this change is impeded by the presence of free nitric acid, and is prevented by the admixture of a small proportion of chloride of mercury. *Iodide or bromide of potassium* gives a yellowish-white precipitate of iodide or bromide of silver, sparingly soluble in ammonia. *Cyanide of potassium* gives a white curdy precipitate of cyanide of silver, which is soluble in excess of the precipitant; phosphoric, chromic, oxalic, tartaric, and citric acids all form insoluble precipitates with salts of silver. Indeed, silver furnishes a greater number of insoluble salts than any other metal; they are almost all neutral in composition, and generally of a dazzling white colour. Most of them, however, blacken when exposed to the action of light. Nearly all of them are soluble in ammonia, and many of them also in nitric acid. *Many metals* reduce solutions of the salts of silver, and throw down the silver from them in a metallic state, as is beautifully shown by the action of mercury, which produces a crystalline deposit of silver, forming what has been termed the *arbor Diana*. Copper and zinc also precipitate silver from its solutions. *Phosphorus* becomes coated with metallic silver if placed in a solution of any of its salts. Solution of *protosulphate of iron* also precipitates silver in the metallic form, from its solutions, if they do not contain free nitric acid.

The tendency of the compounds of silver to form double salts is less strongly marked than among the other noble metals.

(807) *Estimation of Silver*.—Silver may be estimated either in the metallic state, as in the process of cupellation: or in the form of chloride, 100 parts of which, after fusion, correspond to 75.27 of the metal. This precipitation is best effected by acidulating the liquid with nitric acid, and adding hydrochloric acid in slight excess. After the precipitate has been collected and dried, it should be detached from the filter, and fused in a porcelain capsule; on burning the filter, the portions of chloride retained by it are reduced partially to the metallic state by the hydrogen of the paper; the ash must therefore be moistened, first with nitric, and then with hydrochloric acid, to reconvert it into chloride: the excess of acid must afterwards be expelled by heat.

(808) *Separation of Silver from other Metals*.—This is readily effected by means of hydrochloric acid. If lead be present, the solution must be diluted largely: should mercury be in solution, it must be converted into a persalt by boiling the liquid with nitric acid, after which the silver may be precipitated in the form of chloride.

### § III. GOLD.

*Symbol, Au; Equivalent, 196.66; Specific Gravity, 19.34.*

(809) This valuable metal has been prized from the earliest ages of the world. It is found in small quantities in numerous localities, and always occurs in the native state, crystallized in cubes, octohedra, or tetrahedra, or in plates, in ramified masses, and in nodules, which sometimes weigh many pounds. Native gold is always alloyed with silver; small quantities of osmium and iridium, copper, antimony, and sometimes, in a few rare instances, tellurium, are found accompanying it. No regular veins of gold are met with; it commonly occurs either in primitive or volcanic rocks, or in the alluvial deposits of certain rivers. Its most celebrated mines are those of California and Australia; and those of Mexico, Chili, Brazil, and Peru. A good deal of gold is also obtained from the Ural Mountains: many of the rivers of Africa likewise contain it among their sands, as do those of Hungary, Transylvania, and Piedmont. In these countries, it is principally extracted from the river sands by gipsies.

The operations for obtaining gold from its deposits differ from those required by almost every other metal, in being for the most part purely mechanical.

Much of the gold in circulation, previous to the discovery of the deposits in Australia and California, was obtained from auriferous pyrites. This mineral is coarsely pulverized, either before or after roasting, and washed: the heavier particles of gold subside, and are extracted from this concentrated portion by amalgamation, the excess of mercury being separated by distillation. Various methods are adopted for washing the auriferous material: in Mexico this operation is usually performed by negresses, who having pulverized the ore under flat stones, agitate it in wide, shallow, wooden dishes, separating the lighter portions with much dexterity. In Europe, the pyrites is ground and amalgamated, in mills constructed for the purpose. Those who wash the river sands usually select some spot at a bend of the stream, where the mud appears to be black or reddish, as it is here, if anywhere, that the gold is found. The most favourable time is when the waters are subsiding after storms or heavy rains; the sand is concentrated either by washing it in shallow vessels, or else by allowing it to pass through a succession of troughs. Amalgamation is afterwards resorted to and the product is distilled, as in the analogous process for obtaining silver.

(810) *Properties*.—Gold is of a rich yellow colour and high metallic lustre. It is not remarkable for its hardness, being, when in a pure state, nearly as soft as lead. Its tenacity, however, is considerable, ranking next to silver, so that it may be drawn into extremely fine wire. As already mentioned, it is the most malleable of the metals, and so extreme is the thinness to which it may be reduced by hammering, that 200,000 leaves placed one upon another would be required to occupy the thickness of one inch. It fuses at a temperature of  $2016^{\circ}$  F. It cannot be obtained in crystals by cooling, nor can it be advantageously employed for castings, as it shrinks greatly at the moment of solidifying. It is not sensibly volatile in the heat of the furnace, though by a powerful electric discharge, by the concentration of the sun's rays with a large convex lens, or in the intense heat of the oxyhydrogen jet, it may be dispersed in purple vapours. It is one of the most perfect conductors both of heat and of electricity. Gold suffers no change by exposure to air and moisture at any temperature. None of the simple acids, with the exception of the selenic, have any effect upon it, but it is dissolved by any mixture which liberates chlorine. Its usual solvent is aqua regia, which for this purpose is generally prepared by mixing 1 part of nitric acid and 4 parts of hydrochloric acid. The alkalis do not affect it; a crucible of gold is consequently a valuable

instrument in the analysis of minerals which require fusion with the caustic alkalies.

(811) *Preparation of Fine Gold*.—Gold is best obtained in a state of purity by dissolving the metal in aqua regia, and evaporating the solution of chloride of gold thus obtained with an excess of hydrochloric acid, for the purpose of destroying the excess of nitric acid: the solution is then largely diluted with water, and decanted from chloride of silver which is thus precipitated. A solution of protosulphate of iron is next prepared and added to the solution of chloride of gold: 1 part of gold requires between 4 and 5 parts of the crystallized protosulphate. Metallic gold is thus precipitated in the form of a finely divided powder, which when suspended in water, is brown by reflected, but purple when viewed by transmitted light. The reaction which occurs between the chloride of gold and the protosulphate of iron is represented in the annexed equation:  $6(\text{FeO}, \text{SO}_3) + \text{AuCl}_3 = 2(\text{Fe}_2\text{O}_3, 3 \text{SO}_3) + \text{Fe}_2\text{Cl}_3 + \text{Au}$ . For commercial purposes it would be sufficient now to collect the gold, dry it, and after fusing it with borax, to cast it into ingots; but when required to be perfectly free from silver, the gold is not melted at this stage, but the precipitated metal is boiled with hydrochloric acid of sp. gr. 1.1. The acid is decanted, and the residue is boiled twice with fresh acid without washing the gold between these successive additions of acid. The last traces of iron, and nearly all the chloride of silver are thus removed. The gold is then washed, dried, and mixed with its own weight of bisulphate of potash, and fused in a Hessian crucible. The last portions of chloride of silver are thus removed, and the gold is perfectly pure.

Levol prefers to precipitate the gold from an acid solution of its chloride by means of an acid solution of terchloride of antimony:  $3 \text{SbCl}_3 + 2 \text{AuCl}_3 = 3 \text{SbCl}_5 + 2 \text{Au}$ . The hydrochloric solution retains any traces of chloride of silver which may be present.

Gold is used in its finely divided state for gilding porcelain, which is first painted with an adhesive varnish and allowed to become partially dry; the powdered metal is then dabbed on with a dry pencil (having been previously mixed with a fusible enamel), after which the article is fired; the gilt portions are subsequently burnished, and take a high polish. The uses of gold in the fabrication of ornamental articles and in coinage are well known; like silver, it is too soft to be employed in a pure state.



(812) *Gilding* upon metals is effected either through the medium of mercury, as in one of the processes for silvering, or by voltaic action, as in the process of electro-silvering already mentioned; for this purpose, a solution either of the cyanide of gold and potassium, or of oxide of gold in sulphite of potash is used.

About 20 years ago, a means of gilding by immersion was introduced by Mr. Elkington, by which copper trinkets and stamped articles can be coated with a thin film of gold; this method has been very largely practised. The process has been carefully investigated by Barral (*Ann. de Chimie*, III., xviii. 5). The gilding bath is prepared by dissolving 1 part of fine gold in aqua regia, and expelling the excess of acid by evaporation; the chloride is dissolved in a small quantity of water; to this solution 30 parts of bicarbonate of potash are gradually added. This liquid is then mixed with a solution of 30 parts more of the bicarbonate, dissolved in 200 parts of water, and the liquid is boiled for 2 hours: during this operation, the bicarbonate of potash is converted into the sesquicarbonate, and the yellow liquid passes into green; after this, the solution is ready for use. The trinkets having been annealed, are cleansed from adhering oxide by a momentary immersion in a mixture of equal parts of sulphuric and nitric acids; to which, when the gold is intended to have a *dead* appearance, a little common salt is added. The articles are washed in water and then plunged into the gilding liquid, where they are left for about half a minute, after which they are washed in water and dried in hot sawdust. This bath may be also employed for gilding on German silver, platinum, or silver, by immersing the objects composed of these metals in the liquid in contact with wires of copper or of zinc. During this process of gilding, a remarkable reaction occurs,—the gold imparts a portion of its chlorine to the excess of potash contained in the bath, forming chlorate of potash; protochloride of gold is formed and is decomposed by the copper, chloride of copper being produced, whilst metallic gold is deposited upon the surface of the trinkets:  $6 \text{ AuCl}_3 + 6 \text{ KO} + 12 \text{ Cu} = 12 \text{ CuCl} + 5 \text{ KCl} + \text{KO} + \text{ClO}_5 + 6 \text{ Au}$ . During this operation a black powder is precipitated, which contains hydrated carbonate of copper, mixed with a small proportion of the purple of Cassius derived from the action of the gilding solution upon the tin contained in the solder of the trinkets.

With mercury, gold forms a semi-solid amalgam of a yellowish colour, which is soluble in an excess of mercury. This excess may be removed, as in the case of the silver amalgam, by filtering and

squeezing it through chamois leather. It is this amalgam which is formed during the extraction of gold from its ores; it is also extensively prepared for the purposes of gilding. Mr. Henry obtained a combination of mercury with gold ( $\text{Au}, \text{Hg}$ ) crystallized in brilliant 4-sided prisms by acting with dilute nitric acid, aided by a gentle heat, upon an amalgam of gold containing about 1 part of gold to 1000 of mercury. These crystals are insoluble in nitric acid.

(813) *Alloys of Gold*.—The ductility of gold is much impaired by alloying it with other metals, though its hardness and sonorousness are increased: these alloys are generally formed without difficulty. The native alloy of osmium and iridium, however, which frequently accompanies the Californian gold, does not combine with the metal, and remains disseminated throughout in distinct grains after the gold has been melted. These grains occasion much inconvenience; they often escape notice until the metal passes through the coining press, where they make themselves apparent by their hardness, and by the injury which they consequently inflict upon the dies.

Silver and gold may be alloyed in all proportions. In the arts it frequently becomes necessary to separate these two metals and this is usually effected by the method termed *quartation*, or *parting*. This operation depends on the solubility of silver in nitric acid, and the insolubility of gold in this liquid. It is necessary that the silver should amount to at least three-times the weight of the gold, otherwise portions of silver would be mechanically protected from the action of the acid, and the separation would be incomplete. If, therefore, the alloy be found to contain more than  $\frac{1}{3}$  of its weight of gold, sufficient silver is added to reduce it to this proportion, and hence the origin of the term 'quartation'. The metals are fused together, granulated by being poured into water, and they are then digested in the acid. The gold is afterwards melted into ingots, the silver is precipitated as chloride by common salt, and the chloride is reduced either by zinc (797) or by fusion with an alkali (801). Sulphuric acid may be substituted for nitric acid; it is quite as effectual in dissolving the silver, and is much cheaper (803).

The most useful alloy of gold is that which it forms with copper; it is considerably more fusible than pure gold, but is less ductile and malleable. It is this alloy which is used for coinage. English standard gold contains 8.33 per cent of copper, or 11 parts of gold to 1 of copper. The specific gravity of this mixture is

17157, the two metals expanding a little when they unite. In France the standard gold contains 10 per cent. of copper. Jewellers frequently alloy their gold with a mixture of copper and silver. The alloys of gold and copper, when once the materials have been well mixed, do not exhibit the tendency to liquation which occasions so much trouble in the case of silver (794).

(814) *Assay of Gold*.—In the assay of gold, a combination of the processes of cupellation and quartation is employed. In the cupellation of gold the quantity of lead which is needed is about double that employed for silver; 1 part of copper requiring about parts of lead. The assay of gold furnishes results which are more accurate than those obtained in the cupellation of silver. The loss of gold by volatilization is very much smaller, and scarcely any of the metal is carried into the cupel by an excess of lead.

The following is an outline of the method adopted in the assay of gold:—The quantity of the alloy for assay having been accurately weighed, it is wrapped in a piece of paper, with a proportion of silver equal to about 3 times that of the gold which the alloy is supposed to contain,\* and this is submitted to cupellation in the manner already described when speaking of the assay of silver (795). By this means the silver and the gold become thoroughly incorporated, and the copper is oxidized and absorbed by the cupel with the oxide of lead. The auriferous button is then hammered into a flattened disk, about the size of a sixpence, and annealed by heating it to redness. It is next passed between a pair of laminating rollers, by which its thickness is reduced to that of an ordinary address card, after which it is a second time annealed. These operations render it sufficiently flexible to allow of its being coiled into a small spiral by rolling between the finger and thumb. The *coiled* thus obtained is next introduced into a flask which

\* An approximative estimate of the composition of the alloy is sometimes made by the use of the touchstone, though it is seldom employed by the practised assayer. A number of pieces of alloy are formed containing known quantities of gold and copper, or of gold and silver: the first consisting of pure gold; the second of 23 of gold and 1 of copper; the third of 22 of gold and 2 of copper, and so on; the assayer selects one of these alloys, or 'needles,' which from its colour he judges to approach nearest in composition to the alloy which he is about to assay; this he rubs upon a hard, black stone, the 'touchstone,' formerly obtained from Lydia, in Asia Minor; black basalt, however, may be employed for the purpose: the alloy leaves a streak upon the stone, the colour of which is redder in proportion as the copper preponderates. The streak formed by the alloy for assay is then compared with that of the needles, until one of these is found to which it nearly corresponds. The judgment may be further aided by moistening the streaks obtained with a little nitric acid, which attacks the copper or silver, but leaves the gold.

contains about an ounce of nitric acid of sp. gr. 1.180, heated nearly to the boiling point. Brisk evolution of nitrous fumes immediately ensues; the silver is gradually dissolved away, and the gold is left in the form of the original cornet, as a brown, porous, very brittle mass. After this first boiling has been continued for 10 minutes, the flask is removed from the fire, the acid solution is poured off, and the cornet is washed by carefully pouring distilled water upon it; which, after standing for a couple of minutes, is again poured off. Some traces of silver are, however, still retained by the gold, and, in order to remove these, the cornet is again boiled with nitric acid, which, this time, must be of sp. gr. 1.280. In this second boiling, which must be continued for 20 minutes, a small fragment of charcoal should be introduced into the flask, in order to prevent the ebullition from taking place irregularly, with sudden bursts, as it is very apt to do if this precaution be neglected.

The acid having been poured off, the flask is filled up completely with distilled water. A small smoothly finished porous clay crucible is placed over the mouth of the flask, and the flask and crucible are inverted, so that the cornet shall fall gently through the water into the crucible; by a dexterous movement of the hand, the flask is then withdrawn in such a manner as to prevent the overflow of any liquid from the little crucible: the water is afterwards carefully poured off from the cornet, and the crucible is heated to redness in the muffle. By this means the gold, though it is not fused, is rendered much more compact; it shrinks in bulk, loses its brown appearance, and assumes the peculiar colour and lustre of the metal. When cold, the cornet is weighed with the same precision as the original alloy. The assayer calls the arbitrary weight of the alloy upon which he operates 1000; his weights are all subdivided so as to give him the value of the alloy in thousandths of this original quantity; so that if he find a portion of the alloy which originally weighed 1000 of these arbitrary units, to yield a quantity of gold equal to  $916\frac{2}{3}$  of these parts, he reports it as 916.6. 1000 ounces of such an alloy would contain 916.6 ounces of fine gold.

The amount of alloy upon which it is most convenient to operate in assaying is half a gramme, or between 7 and 8 grains.

The gold contained in the cornet is never absolutely pure; it retains a small quantity of lead and of silver, and frequently also traces of copper, which render its weight a little higher than it ought to be. In order to ascertain the amount of this error, a

number of *proofs* are passed through the muffle simultaneously with the alloys, and subjected to the same process as the alloys themselves. These proofs consist of weighed portions of fine gold, to which are added a proportion of copper equal to that estimated to exist in the alloys under examination. The excess of weight which these proofs indicate shows the amount of the correction which it becomes necessary to make. This correction is liable to daily variation, according to the temperature of the furnace, the more or less perfect softening of the buttons during annealing, the thickness of the cornets, &c.; but it usually varies from 0.2 to 0.5 parts in 1000. Most assayers vary the quantity of lead according to the proportion of copper in the alloys. I have found it advantageous to use the same amount of lead in all cases; the correction then becomes uniform for all the assays passed at one operation.

When the alloy contains very little copper, as commonly occurs with native gold, the button of alloy is liable 'to spit' as it cools after the cupellation; this mischance may easily be prevented by the addition of a small fragment of copper, not exceeding  $\frac{3}{4}$  of a grain in weight, previous to introducing the alloy into the cupel.

It frequently happens that it is necessary to ascertain the proportion both of gold and of silver in a given alloy. If the proportion of gold preponderate, the quantity of gold is determined in the manner above described, and that of the gold and silver together is ascertained by submitting a portion of the alloy to cupellation with lead, as if it consisted of silver only (795). The two metals, gold and silver, remain upon the cupel, whilst the copper and more oxidizable metals are absorbed. The weight of the residual button gives the united weight of the gold and silver, and the difference between this weight and that of the gold alone will of course furnish the proportion of silver.

When the proportion of gold is very small compared with that of the silver, the two metals are treated with nitric acid at once (without submitting them to the usual assay for gold); the acid dissolves the silver and other metals which may be present, leaving the gold in the form of a black powder; this powder must be collected by subsidence in one of the small porous crucibles used for annealing gold cornets, in which it is ignited, and can afterwards be weighed without difficulty.

(815) *Oxides of Gold*.—There are two oxides of gold: a protoxide  $\text{AuO}$ , and a teroxide  $\text{AuO}_3$ : the latter possesses acid properties, and is frequently termed auric acid.

The *protoxide* ( $\text{AuO}$ , *Eq.* 204·6), is obtained as a dark green powder by precipitating the protochloride of gold by a dilute solution of potash; it is slightly soluble in excess of the alkali: when digested with ammonia it forms fulminating gold. Protoxide of gold undergoes a kind of solution in pure water, and passes through the filter; but boiling the solution after adding any saline compound causes its precipitation.

*Teroxide of Gold, Auric Acid* ( $\text{AuO}_3$ ), *Eq.* 220·5. — This compound is best obtained by decomposing a solution of the terechloride of gold by magnesia, for if the alkalis be used, they adhere strongly to the precipitate; it falls in combination with the earth, which may be removed by means of dilute nitric acid, and the oxide of gold remains as a yellow hydrate, if the acid used be weak, or as a brown anhydrous oxide if strong; it is very readily reduced by exposure to light, and at a temperature of about  $470^\circ$  it is resolved into metallic gold and free oxygen. It is taken up by strong nitric and sulphuric acids, but no true salts are formed; the oxide is deposited again from these solutions in a pure state on dilution. Teroxide of gold is dissolved by hydrochloric, hydriodic, and hydrobromic acids, forming terechloride, teriodide, and terbromide of gold.

When hydrated it readily combines with the alkalis, forming salts that have been termed *aurates*, which dissolve in water, and form yellow solutions. *Aurate of potash* crystallizes in yellowish needles, ( $\text{KO}, \text{AuO}_3 \cdot 6 \text{aq}$ ). The compounds of auric acid with the earths and other metallic oxides are in most cases insoluble.

Auric acid forms with ammonia a dark olive-brown fulminating compound, analogous to that furnished by silver (799); the same compound may be formed by adding ammonia to the terechloride, but in this case it is of a reddish-yellow colour, owing to the admixture of a little ammoniacal subchloride of gold.

(816) *Bisulphide of Gold*, ( $\text{AuS}_2$ ), *Eq.* 228·6. — When a current of sulphuretted hydrogen is transmitted through a solution of terechloride of gold, a black precipitate is produced, which, according to L  vol, is a bisulphide. It is soluble in the solutions of the sulphides of the alkaline metals: with sulphide of sodium it forms a colourless salt which is soluble in alcohol; it crystallizes in 6-sided prisms, consisting of ( $\text{NaS}, \text{AuS}, 8 \text{HO}$ ; Col. Yorke), the bisulphide of gold having been converted into the protosulphide, whilst the second equivalent of sulphur has entered into combination with the excess of the alkaline sulphide (*Quart. Journ. Chem. Soc.*, i. 242). If finely divided gold be heated with sulphur in contact with car-

bonate of potash, a double sulphide of gold and potassium is formed; it resists a red heat, and is very soluble in water: this sulphur salt is used for gilding china, and produces the colour known as *Burgos lustre*.

(817) *Chlorides of Gold*.—Gold forms two compounds with chlorine,—a protochloride  $\text{AuCl}$ , and a terchloride  $\text{AuCl}_3$ .

*Terchloride of Gold*,  $(\text{AuCl}_3)$ , *Eq.* 303.—This compound is produced when the metal is dissolved in aqua regia; on evaporating the solution to dryness at a temperature not exceeding  $250^\circ \text{F}$ ., this salt remains behind as a red deliquescent mass. It forms with water an orange-coloured solution, which preserves its colour even when very largely diluted; alcohol also dissolves the chloride, and ether takes it up so freely as to separate it from its aqueous solution when agitated with it. Chloride of gold forms a crystalline compound with hydrochloric acid; it also unites with the chlorides of many of the electro-positive metals to form double salts: that with potash crystallizes in efflorescent striated prisms, consisting of  $\text{KCl}$ ,  $\text{AuCl}_3 + 5 \text{ aq.}$ ; that with soda forms 4-sided prisms, with 4 equivalents of water. The chloride of gold is easily reduced by many substances; the reaction of protosulphate of iron has already been mentioned. Oxalic acid produces a similar precipitate of metallic gold; thus,  $\text{AuCl}_3 + 3(\text{HO}, \text{C}_2\text{O}_3) = \text{Au} + 3\text{HCl} + 6\text{CO}_2$ : the powder, when viewed by reflected light, appears of a brown colour, but by transmitted light, whilst suspended in water, it has a purple tint. Many organic substances, if moistened with a solution of the chloride of gold, also exert a reducing effect upon it; hence the fingers or writing paper, if washed over with the solution, become stained of a violet colour when exposed to the sun's light. Metallic gold is also readily obtained from the solution of this salt by other means. A current of sulphurous acid precipitates the gold completely. Phosphorous and hypophosphorous acids, and solutions of their salts, produce the same effect; and a similar result is obtained by contact with many of the metals, such as copper, iron, and zinc. A stick of phosphorus, when immersed in a solution of chloride of gold, soon becomes coated with the reduced metal.

*Protochloride of Gold*,  $(\text{AuCl})$ , *Eq.* 232.0.—When exposed to a gentle heat, the terchloride fuses, without undergoing decomposition; but if the temperature be raised to about  $350^\circ \text{F}$ ., chlorine is gradually expelled, and a pale yellow sparingly soluble powder is left, which is the *protochloride*. It is an unstable compound, but it may be washed with cold water to remove any undecom-

posed, terechloride; boiling water converts it into the terechloride and into metallic gold, and a similar change is produced by exposing it to light. If the temperature be raised a little beyond  $400^{\circ}$ , the whole of the chlorine is expelled.

A *terbromide* of gold may be formed; it crystallizes easily.

There are two *iodides* of gold corresponding to the chlorides. The protoiodide is a pale yellow insoluble powder. The teriodide is soluble, and forms double salts with the alkaline iodides.

(818) *Purple of Cassius*.—When a mixture of protochloride and perchloride of tin very much diluted is added drop by drop to a dilute neutral solution of terechloride of gold, a flocculent purple deposit takes place. The true nature of this compound has been the subject of much discussion. Berzelius concludes from the researches of M. Figuier (*Ann. de Chimie*, III. xi. 354) that it consists of a hydrated double stannate of gold and tin, ( $\text{AuO}$ ,  $\text{SnO}_2 + \text{SnO}$ ,  $\text{SnO}_2 + 4 \text{aq}$ ). The same compound is readily formed by digesting metallic tin in a neutral solution of terechloride of gold; metallic gold and the purple of Cassius being formed. Purple of Cassius undergoes a sort of solution in pure water, and passes through the filter, but it is separated on adding a salt to the liquid and boiling it. It is soluble in ammonia, forming a deep purple solution, and is deposited unchanged if the ammonia be expelled by heat, or neutralized by an acid. Purple of Cassius is decomposed by the acids, but is not changed by the action of light. If heated to redness, water is expelled, and a red powder is left, which is a mixture of metallic gold and peroxide of tin. Purple of Cassius, when mixed with a little borax or some fusible glass, and applied to the surface of china, imparts to it a beautiful rose or a rich purple colour. The red glass of Bohemia owes its colour to this compound.

(819) CHARACTERS OF THE SALTS OF GOLD.—The salts of gold are recognised by the brown precipitate of metallic gold produced by *protosulphate of iron* in their neutral solutions; and by the formation of the purple of Cassius on adding to them a mixture of *protochloride* and *perchloride of tin*. *Metallic tin* yields the same precipitate and is a still more delicate test. Salts of gold are reduced to the metallic state by boiling their acidulated solutions with a soluble *oxalate* or *sulphite*. *Subnitrate of mercury* also gives a dark brown precipitate of reduced gold. All the salts of gold are decomposed when ignited in the open air.

(820) *Estimation of Gold*.—Gold is always estimated in the



metallic state. It may readily be separated from all the preceding metals by precipitating its solution by means of a solution of protosulphate of iron, after acidulating it with hydrochloric acid. The precipitate is collected upon a filter, ignited, and weighed as pure gold.

#### § IV. PLATINUM.

*Symbol, Pt; Equivalent, 98.56; Specific Gravity, 21.5.*

(821) PLATINUM, *little silver*, as its name implies, is a metal which is found in but comparatively few places: it was not recognised as a distinct metal until about a hundred years ago. It always occurs in the native state, usually in small flattened grains, in which it is mixed with palladium, rhodium, osmium, ruthenium, and iridium,—metals which are rarely found except when associated with platinum. Occasionally it occurs in larger nodules, frequently alloyed with gold, copper, iron, and lead. The deposits of platinum are for the most part met with in alluvial districts. Platinum is chiefly supplied from the mines of Mexico, Brazil, and of the Ural Mountains. It is separated by washing from the lighter impurities contained in its ore.

On account of the extreme infusibility of platinum, it requires a mode of manipulation which is complicated and peculiar. The method which is employed was contrived by Dr. Wollaston:—The ore is digested in diluted aqua regia, as long as anything is dissolved, the solution of the platinum taking place very slowly; the clear liquid is then decanted, and a solution of sal ammoniac is poured into it; the greater part of the platinum is thus precipitated in the form of a yellow double salt ( $\text{NH}_4\text{Cl}$ ,  $\text{PtCl}_2$ ), which is sparingly soluble. The mother liquor still retains a portion of platinum, which is precipitated by means of metallic iron; the black powder is redissolved in aqua regia, and precipitated by the addition of sal ammoniac; the double salt thus obtained being added to the first crop. The chloride of platinum and ammonium is then washed, and heated to redness; by which means the ammonia and chlorine are expelled, leaving the platinum behind in porous slightly coherent masses: this *spongy platinum* is powdered in a wooden mortar and rubbed into a magma with water, in which state it is thoroughly washed; the metallic particles soon subside, and the lighter impurities are carried away. This metallic mud is then poured into a somewhat conical brass mould, closed below with blotting paper loosely supported by a plug; the greater

part of the water drains off, and the whole is then subjected to the action of a very powerful press. • The mass which previously was of a dull grey colour, now assumes a compact metallic appearance, and acquires a specific gravity of about 10; it is next exposed to an intense heat in a wind furnace, and the ingot is forged by hammering it upon its two ends,—never upon its sides, as if this were done it would split. This heating and forging is several times repeated until it becomes homogeneous and ductile; it then has a specific gravity of about 21.5. . . .

(822) *Properties*.—Platinum is a white metal susceptible of high lustre, and possessed of considerable hardness. In ductility it rivals iron and surpasses all other metals, and in tenacity it is inferior only to iron, and perhaps copper. It resists the highest heat of the forge, and can only be fused by the voltaic battery or by the oxyhydrogen blowpipe, before which it is volatilized and burns with scintillations. The process now employed for working it depends upon its property of welding at very high temperatures. Attempts to crystallize it artificially have not succeeded, but very perfect octohedra have been met with in its native beds. Its specific gravity differs somewhat with the mode of manipulation to which it has been subjected, but it varies between 21 and 22, being (with the exception of iridium, which is equally dense), the heaviest form of matter as yet known. In its power of conducting heat and electricity it is much inferior to gold and silver, in these respects ranking very near to iron.

Platinum does not undergo oxidation in air at any temperature; none of the acids have singly any effect upon it; aqua regia dissolves it, though but slowly. If heated to redness in air in contact with the alkalies or alkaline earths, especially with lithia or baryta, it is corroded, owing to the formation of an oxide which combines with the alkaline base. When phosphorus is heated with spongy platinum, combination takes place between them readily. The affinity of sulphur for platinum is much less powerful. Dry chlorine is without action upon this metal, even when aided by heat.

(823) Platinum may be obtained in a state of subdivision still finer than that in which it is left on heating the double chloride of platinum and ammonium. In this form it has the appearance of soot, and is termed *platinum black*. It may be procured in this condition by dissolving the protochloride of platinum in a strong solution of caustic potash, and adding alcohol to the hot liquid which is placed in a capacious vessel, and kept constantly stirred: brisk effervescence takes place, owing to the escape of carbonic acid; the

platinum is reduced, and is deposited as a black powder, which requires repeated washing,—first with alcohol, next with potash, then with hydrochloric acid, and lastly with water. Platinum, in this finely divided state, greedily condenses oxygen from the air, and absorbs many times its bulk of the gas. If moistened with alcohol or ether it imparts this oxygen to them, and forms new compounds; whilst the powder glows from the heat which is extricated. In all its states, platinum possesses, in a marked degree, this property of condensing gases upon its surface; and the more finely it is divided, and consequently the larger the surface which it presents, the more striking is the phenomenon.

(824) *Uses.*—The most important applications of platinum are confined to the laboratory of the manufacturing and experimental chemist; they depend upon its great infusibility and its power of resisting chemical agents. Its introduction as a material for the construction of apparatus employed by the analytical chemist, has contributed in no small degree to the rapid progress of the science during the last 40 or 50 years, by conferring upon his experiments a precision, neatness, and accuracy till then unattainable. In the concentration of oil of vitriol, large platinum stills are frequently employed; some of these vessels weigh upwards of 1000 ounces. An attempt was made in Russia to employ platinum for coinage, but it was found to be inconvenient, and the experiment has been abandoned.

*Alloys.*—Platinum may be easily alloyed with many metals, the combination generally taking place with the extrication of light and heat: these alloys are much more fusible than pure platinum. Care must therefore be taken not to heat the oxides of fusible and easily reduced metals, such as lead or bismuth, in platinum crucibles, as if the oxides should happen to be reduced, the crucible would be destroyed by the formation of a fusible alloy. Most of the platinum of commerce is said to contain iridium, which without impairing its power of resisting chemical agents, increases its hardness and durability. It is remarkable, that though pure platinum is perfectly insoluble in nitric acid, yet when alloyed with 10 or 12 times its weight of silver, both metals are easily and completely dissolved by it. An amalgam of platinum may be formed, by acting upon an amalgam of sodium with a neutral solution of the double chlorides of platinum and sodium: when this amalgam is attacked by nitric acid, the platinum according to Levol, is partially dissolved as well as the mercury.

Platinum enters into combination with carbon and with silicon : sometimes in the combustion of ordinary platinum wire before the blowpipe, the globules are covered with a film of colourless glass, arising from the oxidation of the silicon and the fusion of the resulting silica. A brittle granular compound of platinum and silicon was accidentally obtained by Professor Daniell, owing to the action of silicon at a high temperature upon one of the platinum bars of his pyrometer. It appeared to be formed by a kind of cementation, the silicon being derived from the clay of the envelope in which it was heated : the proportion of silicon amounted to 1.5 per cent. .

(825) *Oxides of Platinum*.—There are two oxides of platinum, a protoxide and a binoxide. The *protoxide* ( $\text{PtO}$ ; *Eq.* 106.5) is procured by digesting the protochloride of the metal in a solution of potash : a dark olive-green liquid is thus obtained owing to the solution of the oxide in the excess of alkali. On neutralizing the solution with sulphuric acid, a black hydrated protoxide of platinum subsides. It is slowly dissolved by acids forming unstable salts with them, and is readily decomposed by heat.

The *Binoxide* ( $\text{PtO}_2$ , *Eq.* 114.5), has a strong tendency to combine with alkaline bases ; it is therefore prepared by adding to a solution of nitrate of platinum one half of the quantity of carbonate of soda which is necessary for its complete precipitation. It is thus procured as a voluminous brown hydrate, from which water is expelled at a gentle heat, and the mass becomes darker ; a higher temperature expels the whole of the oxygen. Hydrated oxide of platinum is soluble in solutions of potash and soda ; the compounds thus formed may be obtained in crystals. The soda compound consists of  $(\text{NaO}, 3 \text{ PtO}_2 + 6 \text{ aq})$ . Binoxide of platinum also enters into combination with other bases, forming compounds most of which are insoluble.

The oxide is also soluble in acids, and forms well characterized salts, the solutions of which have a yellowish-brown colour.

(826) *Sulphides of Platinum*.—Platinum combines with sulphur in two proportions. The *protosulphide* ( $\text{PtS}$ ) may be obtained as a black precipitate by passing sulphuretted hydrogen over moistened protochloride of platinum ; by heating sulphur with the double chloride of platinum and ammonium it is left as a grey powder of metallic appearance, from which the sulphur is completely expelled by heating it in the open air.

The *Bisulphide* ( $\text{PtS}_2$ ) is best procured by decomposing the double chloride of sodium and platinum by sulphuretted hydrogen ;

it falls as a dark-brown powder, which becomes black during desiccation. It is somewhat soluble in the sulphides of the alkaline metals. By ignition in close vessels it is converted into protosulphide. When exposed to the air, and gently heated, it is partially converted into sulphate, but at a higher temperature is wholly decomposed, metallic platinum remaining.

(827) *Chlorides of Platinum*.—These correspond in number and composition to the sulphides and oxides of the metal. In order to procure the *protochloride* ( $\text{PtCl}$ , *Eq.* 134), the solution of platinum in aqua regia should be evaporated, and the residue exposed to a heat of  $450^\circ$ , as long as any chlorine is expelled; the compound which remains is the protochloride. It is of an olive colour, and is insoluble in water: it is scarcely acted upon by nitric and sulphuric acids; hydrochloric acid dissolves it sparingly; but it is dissolved easily by caustic potash, and by the bichloride of platinum, with which latter it forms a double salt. It forms double crystallizable salts with the alkaline chlorides.

The *Bichloride of Platinum* ( $\text{PtCl}_2$ , *Eq.* 169.5) is obtained by dissolving platinum in aqua regia, and evaporating the solution to dryness by means of a steam heat. It is a deliquescent salt, and forms a deep orange-coloured solution in water, from which it may be obtained crystallized in prisms: it is also dissolved largely by alcohol and by ether. When heated to  $450^\circ$  it loses half its chlorine, forming the protochloride, and if the temperature be further raised, it is completely decomposed, and metallic platinum is left.

With other chlorides it forms numerous double salts, which are produced by mixing the solutions of these chlorides with that of the bichloride of platinum, and evaporating. The double chloride with potassium ( $\text{KCl}$ ,  $\text{PtCl}_2$ , *Eq.* 244) is a sparingly soluble anhydrous compound, which crystallizes in octohedra; it is insoluble in alcohol and ether. This salt is commonly used as a means of determining analytically the quantity of potash in a compound. It is decomposed, by a red heat, into chloride of potassium and metallic platinum.

The double *chloride of platinum and sodium* ( $\text{NaCl} + \text{PtCl}_2 + 6 \text{ aq}$ ) crystallizes in beautiful red striated prisms, which are soluble in water, alcohol, and ether. With *chloride of ammonium* ( $\text{NH}_4\text{Cl}$ ,  $\text{PtCl}_2$ ), a compound is formed very similar in appearance to that with potassium, with which it is isomorphous. It is sparingly soluble in water, and is insoluble in alcohol and ether. This salt is employed in analysis for determining the quantity of ammonia present in solutions. It is also made use of for separating

platinum from the other metals with which it is associated, after they have been brought into solution by treating the ore with aqua regia (821). When the double chloride of platinum and ammonium is ignited, the ammonia and chlorine are wholly expelled, and pure platinum remains.

(828) *Ammoniacal derivatives from the Chlorides of Platinum.*—The action of ammonia upon the chlorides of platinum gives rise to the formation of several remarkable compound bases, the composition of which offers considerable interest in a theoretical point of view. Magnus found that if the protochloride of platinum be dissolved in hydrochloric acid, the addition of an excess of ammonia to the boiling solution causes the deposition of brilliant green acicular crystals which are insoluble in water and in hydrochloric acid: they consist of the elements of 2 equivalents of protochloride of platinum and 2 equivalents of ammonia ( $\text{Pt}_2\text{Cl}_2\text{N}_2\text{H}_6$ ). This compound, however, undergoes no change when digested at ordinary temperatures in solution of the caustic alkalis, or in the concentrated acids, but when boiled with them it is slowly decomposed. If digested in nitric acid, one-half of the platinum is separated in the metallic state, and on evaporating the solution, a salt is obtained crystallized in small flattened prisms ( $\text{PtCl}_2 \cdot 2 \text{H}_3\text{N} \cdot \text{O}$ ) $\text{NO}_5$ . Neither the chlorine nor the platinum can be detected in this solution by the usual tests. The nitric acid may be displaced from it by double decomposition with sulphate, phosphate, or oxalate of soda, and a sparingly soluble sulphate, phosphate, or oxalate of the base is then formed. The base of these salts (commonly called *Gros's salts*, from the name of their discoverer) has not been isolated.

Raewsky discovered that if the green salt of Magnus be boiled with an excess of nitric acid, red fumes are disengaged, and a different salt is formed, which may be obtained in crystals on evaporation. The nitric acid may be displaced from this compound by an equivalent quantity of oxalic or carbonic acid.

It would only perplex the student to detail the methods of preparing the various compounds of this class, which subsequent inquiries have brought to light; indeed, the examination of these salts is yet far from complete. The following table contains the formulæ of the principal series which have been ascertained to exist:\*

\* The following papers may be consulted upon this subject: Gros, *Ann. de Chimie*, II., lxxix. 204; Reiset, *Ib.*, III., xi. 417; Raewsky, *Ib.*, III., xxii. 278; Peyrone, *Liebig's Annal.* li. 1, and lv. 205; Gerhardt, *Comptes Rendus des travaux de Chimie*, par Laurent et Gerhardt, 1849, pp. 113, and 273.

1. *Salts of Platosamine* (Reiset's second base).

Platosamine . . . . .	$\text{PtH}_3\text{N}, \text{O}.$
Hydrochlorate of platosamine (yellow) . . . . .	$\text{PtH}_3\text{N}, \text{Cl}.$
Nitrate of platosamine . . . . .	$\text{PtH}_3\text{N}, \text{O}, \text{NO}_5.$

2. *Salts of Diplatosamine* (Reiset's first base).

Diplatosamine . . . . .	$\text{PtH}_6\text{N}_2, \text{O} + \text{HO}.$
Hydrochlorate of diplatosamine . . . . .	$\text{PtH}_6\text{N}_2, \text{Cl}.$
Magnus's green salt . . . . .	$\text{PtH}_6\text{N}_2\text{Cl} + \text{PtCl}.$
Nitrate of diplatosamine . . . . .	$\text{PtH}_6\text{N}_2\text{O}, \text{NO}_5.$
Bicarbonate of diplatosamine . . . . .	$\text{HO}, \text{PtH}_6\text{N}_2\text{O}, 2 \text{CO}_2.$

3. *Salts of Platinamine* (Gerhardt's base).

Platinamine . . . . .	$\text{PtH}_3\text{N}, \text{O}_2.$
Bihydrochlorate of platinamine . . . . .	$\text{PtH}_3\text{N}, \text{Cl}_2.$
Neutral nitrate of platinamine . . . . .	$\text{PtH}_3\text{N}, \text{O}_2, \text{NO}_5, 3 \text{HO}.$
Binitrate . . . . .	$\text{PtH}_3\text{N}, \text{O}_2, 2 \text{NO}_5.$

4. *Salts of Diplatinamine.*

Diplatinamine (not isolated)	
Hydrochlorate of diplatinamine . . . . .	$\text{PtH}_6\text{N}_2, \text{Cl}.$
Neutral nitrate . . . . .	$\text{PtH}_6\text{N}_2\text{O}_2, \text{NO}_5, \text{HO}.$
Sesquinitrate . . . . .	$2(\text{PtH}_6\text{N}_2\text{O}_2), 3\text{NO}_5, \text{HO}.$

5. *Salts obtained by Gros.*

Base not isolated . . . . .	$\text{PtClH}_6\text{N}_2\text{O}.$
{ Hydrochlorate . . . . .	$\text{PtClH}_6\text{N}_2\text{Cl}.$
{ (viewed by Gerhardt as bihydrochlorate)	
{ of diplatinamine) . . . . . }	$\text{PtH}_6\text{N}_2\text{Cl}_2.$
Nitrate . . . . .	$\text{PtClH}_6\text{N}_2\text{O}, \text{NO}_5.$

6. *Salts obtained by Raewsky.\**

Base not isolated	
Binitrate (crystallized) . . . . .	$\text{Pt}_2\text{ClH}_{12}\text{N}_4\text{O}_5, 2 \text{NO}_5.$
Phosphate . . . . .	$\text{Pt}_2\text{ClH}_{12}\text{N}_4\text{O}_5, \text{PO}_5, \text{HO}.$
Bicarbonate . . . . .	$\text{Pt}_2\text{ClH}_{12}\text{N}_4\text{O}_5, 2 \text{CO}_2.$

Gerhardt disputes the correctness of Raewsky's formulae, and regards the salts discovered by this chemist as sesquiacid salts of diplatinamine, and he views those of Gros as biacid salts of diplatinamine, in some of which two acids are present. A serious objection to this supposition, however, is afforded by the fact that Gros's hydrochlorate abandons only half its chlorine when mixed with the solution of nitrate of silver. It ought to give up the whole were Gerhardt's theory correct.

A very ingenious theory of the composition of the four first bases has been proposed by the same chemist. He supposes platinum, in common with several other metals (such as mercury, iron, palladium and cobalt), to have

(829) The *Bibromide of Platinum* is a brown insoluble powder. A *Bimodide of Platinum* is precipitated as a sparingly soluble powder of a deep wine-red colour, on adding iodide of potassium to a dilute solution of chloride of platinum.

*Fulminating platinum* is procured as an insoluble black powder by precipitating the sulphate with an excess of ammonia. The acids decompose it with formation of ammoniacal salts. If suddenly heated to about  $400^{\circ}$  it explodes. The *persulphate* of platinum may be formed by treating the bisulphide with fuming nitric acid, and heating, to expel the excess of nitric acid. The *pernitrate* may in like manner be formed by digesting the bioxide in diluted nitric acid; both these salts form insoluble double subsalts on the addition of an alkali.

(830) CHARACTERS OF THE SALTS OF PLATINUM.—The proto-salts of platinum are unimportant. Of the persalts of platinum the bichloride is the only soluble compound of frequent occurrence. These salts are distinguished by the following characters. When heated they are all decomposed, and leave a residue of metallic platinum: they have a brownish-yellow colour in solution. With *potash*, or with any of its salts, they give a yellow precipitate of

the power of entering into combination with two different equivalent numbers; one of these is the number 99, ordinarily assumed as the equivalent of the metal (which he terms *platinosum*), having a symbol Pt. The other equivalent is equal to one-half of this, or 49.5, its symbol being pt, or ( $\frac{1}{2}$  Pt). The compound usually known as protochloride of platinum ( $\text{PtCl}$ ), Gerhardt terms *chloride of platinosum*; and the salt ordinarily described as bichloride of platinum,  $\text{PtCl}_2$ , he designates as *chloride of platinumum* ( $\text{ptCl}$ ) or ( $\frac{1}{2}$  Pt, Cl).

The different platinum bases are viewed by Gerhardt as compound ammonias in which a portion of the hydrogen is displaced by platinum. The salts of platosamine, as well as those of diplatosamine, require 1 equivalent of an acid for their neutralization; they each contain 1 equivalent of platinosum, this being the element which confers upon them their basic power. The salts of platinamine, and of diplatinamine, on the other hand, are supposed to contain 2 equivalents of platinumum; and thus the necessity for 2 equivalents of acid in order to neutralize these bases is explained. The following table, which represents the compounds formed by these different bases with hydrochloric acid, will illustrate this theory.

Chlorides of Platinum Bases.	By Gerhardt's Theory.	Empirical Formula.
Hydrochlorate of Platosamine . .	$\text{PtH}_2\text{N}, \text{HCl}$ . .	$\text{PtH}_2\text{NCl}$ .
Diplatosamine . .	$\text{PtH}_6\text{N}_3, \text{HCl}$ . .	$\text{PtH}_6\text{N}_3\text{Cl}$ .
Platinamine . .	$(\frac{1}{2}\text{Pt})_2\text{H}_2\text{N}, 2 \text{HCl}$ . .	$\text{PtH}_2\text{NCl}$ .
— Diplatinamine . .	$(\frac{1}{2}\text{Pt})_2\text{H}_4\text{N}_2, 2 \text{HCl}$ . .	$\text{PtH}_4\text{N}_2\text{Cl}_2$ .

This theory of the existence of two different equivalents of platinum, adapts itself very happily to the case which we are now considering, but when the attempt is made to generalize it, by assuming that iron, copper, &c., also have two different equivalents, it is open to very serious objections, which are fatal to its general adoption.



the double chloride of platinum and potassium, which is soluble in a large excess of this alkali: *soda* precipitates a brown hydrated oxide which is soluble in excess of the alkali: with *ammonia*, or a soluble salt of ammonia, a yellow double chloride is precipitated, which is decomposed by heat, leaving metallic platinum. *Sulphuretted hydrogen* and *hydrosulphate of ammonia* give a black sulphide, which is soluble in a large excess of the alkaline sulphides.

Solutions of the salts of platinum are reduced by the *subnitrate of mercury*, but not by *protosulphate of iron*. *Protochloride of tin* produces a very deep brown solution, but yields no precipitate; *iodide of potassium* gives a brown precipitate of iodide of platinum. The solutions of the salts of platinum are readily reduced to the metallic state by means of *zinc* or *iron*.

(831) *Estimation of Platinum*.—Platinum may be estimated either in the metallic state, or in the form of a double chloride of platinum with potassium or ammonium. The solutions from which these double salts are precipitated should be concentrated; the complete separation of the salt is favoured by the addition of alcohol, and the washing of the precipitate should be performed with dilute alcohol. Platinum may thus be separated from all the metals hitherto described: 100 parts of the double chloride of platinum and potassium contain 40.43 of the metal; and 100 parts of the ammonia salt contain 44.28 of platinum.

## § V. PALLADIUM.

*Symbol*, Pd; *Equivalent*, 53.24; *Specific Gravity*, 11.8.

(832) PALLADIUM is one of the rare metals which occur chiefly in the ore of platinum, in which it was discovered by Dr. Wollaston in the year 1803. It usually forms from 1 to  $\frac{1}{2}$  per cent. of these ores. According to G. Rose palladium is amorphous, as it is found native in cubes, and in 6-sided plates. In order to extract the metal from the ore of platinum, the solution of this ore in aqua regia is treated with chloride of ammonium to separate the platinum, as already described (821), and to the filtered liquid, cyanide of mercury in solution, is added; a white flocculent cyanide of palladium subsides; this is converted into a sulphide by heating it in contact with sulphur, and the sulphur is subsequently expelled by repeated roastings. Another source of palladium is the native alloy which it forms with gold, and which is found in the Brazilian mines. In order to extract the palladium from it, Mr. Cock directs the alloy to be fused with silver, and then boiled

in nitric acid, by which all the metals except the gold are brought into solution. The decanted liquid is then to be mixed with a solution of common salt by which the whole of the silver is thrown down in the form of chloride. Palladium with the other metals (which consist principally of copper, with some lead and iron,) still remains dissolved. Bars of metallic zinc are introduced into the liquid, and these metals are precipitated upon the zinc in the form of a black powder, consisting of reduced metal. This precipitate is washed, and redissolved in nitric acid, supersaturated with ammonia, which dissolves the oxides of palladium and copper, while those of iron and lead are precipitated: the clear liquid is now supersaturated by hydrochloric acid. Palladium is thus thrown down in the form of a yellow, sparingly soluble double chloride of palladium and ammonium; by ignition it is reduced, and agglutinates, but does not fuse. A small quantity of palladium still remains in solution, and may be recovered by the introduction of bars of iron.

Palladium is a white, hard metal possessed of considerable ductility and tenacity. It is not fusible in an ordinary wind furnace, but melts at a lower temperature than platinum. Before the oxyhydrogen blowpipe it burns with scintillation. It undergoes no change in the open air at ordinary temperatures; but at a low red heat it becomes covered with an iridescent film owing to a superficial oxidation; on increasing the heat, the oxygen is expelled, and the metal resumes its brilliant surface. Palladium is dissolved when heated in nitric acid or in aqua regia, but it is acted upon by the other acids with difficulty. By fusion with nitre or with the alkalies it is oxidized. If a solution of iodine in alcohol be evaporated on a slip of palladium a stain is left, by which this metal is at once distinguished from platinum. Palladium readily combines with gold, which is rendered brittle by its presence even in small proportion. It has a remarkable power of whitening the colour of gold, even though present in the mixture only in small quantity; and when it forms 20 per cent. of the mass, the alloy is quite white. If alloyed with twice its weight of silver it forms a ductile compound which is well adapted for the construction of small weights. Palladium has been applied in a few cases to the construction of graduated scales for astronomical instruments, for which, by its whiteness, hardness, and inalterability in air, it is well adapted.

(833) *Oxides of Palladium*.—This metal appears to form 3 oxides: a protoxide, which is the base of the salts of the metal;

a binoxide, and a suboxide,\*  $\text{Pd}_2\text{O}$ , which, according to Kane, is obtained by heating the hydrated protoxide to incipient redness.

The *protoxide* ( $\text{PdO}$ , *Eq.* 612) may be procured as a black powder, by heating the nitrate to low redness; or it may be obtained upon adding carbonate of potash or soda to its salts, as a dark brown hydrate from which the water may be expelled by heat. At a bright red heat it loses its oxygen.

The *binoxide* is prepared by decomposing the solid double chloride of palladium and potassium by solution of potash; it forms a yellowish-brown hydrate, which is soluble in the alkalies; but it becomes anhydrous by boiling it with water, and is then deposited as a black powder.

*Sulphide of Palladium* ( $\text{PdS}$ ), may be formed either directly, by heating powdered sulphur with palladium, or by precipitating the salts of the metal by sulphuretted hydrogen; it forms a fusible greyish-white lustrous mass, from which heat expels the sulphur.

If a piece of palladium foil or wire be held in the flame of a spirit lamp, soot is speedily deposited in large quantity, the foil or wire is corroded, and the mass of soot is found to contain palladium throughout, owing to the formation of a carburet of the metal.

(834) *Chloride of Palladium* ( $\text{PdCl}$ ) is obtained by evaporating to dryness a solution of palladium in aqua regia; it forms brown hydrated crystals, which become black when the water is expelled; if heated to redness metallic palladium is left. Chloride of palladium forms double salts with the soluble chlorides; those with potassium and ammonium are yellow. With ammonia, chloride of palladium forms a series of compounds analogous to those of platinum (828): one of them, palladamine ( $\text{PdH}_3\text{N})\text{O}$ , is a powerfully alkaline base. The *bichloride* exists in solution in aqua regia, but cannot be obtained in crystals: it forms double salts with the alkaline chlorides; the double salt with potassium crystallizes in ruby-red prisms.

Cyanogen has a stronger affinity for palladium than for any other metal. This cyanide is procured as a yellowish precipitate by adding cyanide of mercury or of potassium, to neutral solutions of any of the salts of palladium: it forms a series of double cyanides.

The *Sulphate of Palladium*, ( $\text{PdO}, \text{SO}_3$ ) may be obtained by decomposing the nitrate by sulphuric acid, or by dissolving the oxide in sulphuric acid. It is a deliquescent salt which forms a deep brownish-red solution; when heated it loses acid, and forms a subsalt.

The *nitrate* is formed by boiling nitric acid on palladium; it

may be obtained in rhomboidal prisms; they are freely soluble in water, and form a deep red liquid. If ammonia in excess be added to this solution, an ammoniacal nitrate of palladium may be crystallized from it in rectangular tables.

(835) CHARACTERS OF THE SALTS OF PALLADIUM.—The compounds of palladium are distinguished by the yellowish precipitate of cyanide of palladium, formed on adding *cyanide of mercury* to their neutral solutions. The *alkalies* precipitate the compounds of palladium in the form of a red or orange subsalt, which is soluble in excess of the alkali by the aid of heat. *Ammonia* gives a flesh-coloured precipitate, soluble in excess of ammonia. *Iodide of potassium* precipitates a black iodide of palladium. *Sulphuretted hydrogen* and *hydrosulphate of ammonia* throw down a black sulphide of palladium, insoluble in the alkaline sulphides. Concentrated solutions of the salts of palladium are reduced by solution of *protosulphate of iron*, and by many of the metals. *Protochloride of tin* produces a black precipitate, which is dissolved by hydrochloric acid, forming an intense green solution.

Palladium may be separated from all other metals, except copper and lead, by the addition of the cyanide of mercury to the solution previously neutralized by means of carbonate of soda. The cyanide of palladium when ignited in the air leaves metallic palladium.

## § VI. RHODIUM.

*Symbol*, Ro; *Equivalent*, 52.16; *Specific Gravity*, 11.2.

(836) RHODIUM usually forms about  $\frac{1}{2}$  per cent of the ore of platinum; it may be extracted from the solution in aqua regia after the separation of the platinum and palladium by sal ammoniac and cyanide of mercury: the excess of cyanide of mercury is then decomposed by acidulating the solution with hydrochloric acid, adding common salt and evaporating to dryness; the chloride of sodium thus forms double chlorides with all the metals in solution; the residue is treated with alcohol, which dissolves all these double salts, except that of sodium and rhodium, which remains behind as a red powder; this is dissolved in water, and the rhodium thrown down in a pulverulent form by means of bars of metallic zinc. The chloride of sodium and rhodium may also be decomposed by heating it in a current of hydrogen gas, when, on washing the mass with water, the rhodium is left in a pulverulent form.

Rhodium is a very hard, white, and brittle metal; with the

exception of iridium, it is the least fusible of the metals. When pure, it is insoluble in the acids, though if alloyed with platinum, copper, or bismuth, it is dissolved with them in nitrohydrochloric acid. Rhodium has a considerable affinity for oxygen, and may be oxidized by fusion with nitre and carbonate of potash; bisulphate of potash also oxidizes the metal and forms a soluble double sulphate of rhodium and potassium. If heated in contact with chloride of sodium, in a current of chlorine, a soluble double chloride of sodium and rhodium is produced.

The only use to which rhodium has hitherto been applied is to the formation of nibs for metallic pens, for which it is well fitted from its extreme hardness and inalterability.

(837) Rhodium appears to form two definite *oxides*,  $\text{RO}$  and  $\text{R}_2\text{O}_3$ , besides some compounds intermediate between them. The *protoxide* has not been obtained in a state of purity.

*Sesquioxide of Rhodium* ( $\text{R}_2\text{O}_3$ ) *Eq.* 60·12. This is the only salifiable oxide of rhodium; it may be procured by heating rhodium with nitre and carbonate of potash; the oxide forms an insoluble compound with potash, which is to be well washed, and decomposed by digestion with hydrochloric acid: the sesquioxide is thus left as a greenish-grey hydrate which is insoluble in all acids.

Rhodium forms two *sulphides*,  $\text{RoS}$  and  $\text{Ro}_2\text{S}_3$ .

If the metal be heated in the vapour of sulphur, the two bodies unite with incandescence, and form the *protosulphide*, which has a bluish-grey colour, and fuses at a very high temperature; the sulphur burns off in the open air and leaves a forgeable mass of metallic rhodium. The *sesquisulphide* may be obtained in the form of a brown hydrate by decomposing a hot solution of the double chloride of sodium and rhodium by means of an alkaline sulphide.

Three *chlorides of rhodium*,  $\text{RoCl}$ ,  $\text{Ro}_4\text{Cl}_6$ , and  $\text{Ro}_2\text{Cl}_3$  are stated by Berzelius to exist, but the sesquichloride is the only one of importance. The *sesquichloride* is formed by decomposing the chloride of potassium and rhodium by silicofluoric acid, which separates the potassium as a gelatinous silicofluoride; the filtered liquid when evaporated to dryness, leaves the sesquichloride of rhodium. This chloride unites with many of the soluble chlorides to form crystallizable double salts, which are of a ruby or rose colour (whence the metal receives its name); that of sodium crystallizes in cubes or in octohedra, which are efflorescent in the air ( $3 \text{ NaCl}$ ,  $\text{R}_2\text{Cl}_3$  + 18 aq); they are insoluble in alcohol.

(838) *CHARACTERS OF THE SALTS OF RHODIUM.*—The double chloride of sodium and rhodium is the best known of these compounds. The salts of the sesquioxide of the metal generally form

rose-coloured solutions; they are decomposed by *iron* or *zinc*, which causes a deposit of metallic rhodium. *Potash* occasions a precipitate of yellow hydrated oxide, soluble in the excess of the alkali. *Iodide of potassium* throws down a yellow iodide of rhodium. *Sulphuretted hydrogen* slowly forms a brown precipitate insoluble in the alkaline sulphides. The *soluble sulphites* give a pale yellow precipitate.

## VII. RUTHENIUM.

*Symbol*, Ru; *Equivalent*, 52.11; *Specific Gravity*, 8.6.

(839) *Treatment of the Platinum Residue*.—After the platinum ore has been exhausted with aqua regia, a residue is obtained which frequently contains both titaniferous iron and chrome iron, but its most important constituent is an alloy in flat plates or scales, of a white colour and metallic lustre. This is usually considered to be an alloy of osmium and iridium. It has, however, recently been found to consist of four metals—viz., osmium, iridium, ruthenium, and a small quantity of rhodium.

Fremy has lately simplified the method of separating the different metals contained in this residue: and for this purpose he avails himself of the oxidability of osmium and the volatility of its peroxide. His mode of proceeding consists of a process of roasting the alloy in a current of dry air (*Chem. Gaz.*, 1854, p. 241). For this purpose the residue is placed in a porcelain or platinum tube, and heated to redness. In the portion of the tube which projects from the furnace some fragments of porcelain are placed, and the tube is connected with a series of glass flasks for the purpose of condensing the osmic acid as it distils; in the last flask a solution of potash is placed, in order to retain such portions of osmic acid as may have escaped condensation; and this flask is connected with an aspirator, by means of which a current of atmospheric air is maintained through the apparatus. The air is dried, and freed from organic particles before it enters the heated tube, by causing it to pass through tubes filled with pumice moistened with sulphuric acid. During the operation the osmium and ruthenium become oxidized. The osmic acid condenses in beautiful needles in the flasks, and mechanically carries forward the oxide of ruthenium, which is deposited upon the fragments of porcelain in regular crystals.

The fixed residue consists of an alloy of iridium and rhodium, mixed with a little osmium and ruthenium. This is to be fused

with caustic potash, by which the oxide of ruthenium is removed and is dissolved out on washing the fused mass with water. The undissolved portion is ignited with four parts of nitrate of potash, and the product is treated with boiling water, which dissolves the osmium, and on cooling, often deposits it in octohedral crystals of osmite of potash. The residue now contains only sesquioxides of iridium and of rhodium. Aqua regia, when boiled upon it, converts most of the iridium into the soluble bichloride; a solution of chloride of potassium is added to the liquid, after which crystals of the double chloride of iridium and potassium are deposited as it cools. The sesquioxide of rhodium, which is insoluble in aqua regia, is converted into a soluble double salt by mixing it intimately with chloride of sodium and heating the mass to dull redness in a current of dry chlorine.

(840) RUTHENIUM is a metal which, in 1845, was shown by M. Claus to exist in the ore of platinum. It is very hard, and brittle, and is infusible even before the oxyhydrogen blowpipe. It absorbs oxygen at a red heat, and the oxide so obtained is not decomposed by simple elevation of temperature. The metal is readily oxidized by fusion with nitre, or with caustic potash. Ruthenium accompanies the alloy of osmium and iridium, and is not found in the portion of platinum ore which is soluble in aqua regia. It is most easily obtained by Fremy's process (839). The sesquioxide of ruthenium is not volatile when heated alone, but is carried forward mechanically by the peroxide of osmium, and condenses in crystals near to the source of heat. By heating this oxide in a current of hydrogen, the metal is obtained in the form of a dark grey powder. Ruthenium forms four compounds with oxygen,  $\text{RuO}$ ,  $\text{Ru}_2\text{O}_3$ ;  $\text{RuO}_2$  and  $\text{RuO}_3$ .

*Ruthenic acid* ( $\text{RuO}_3$ ) is an insoluble metallic acid; it may be obtained by heating any of the preceding oxides with nitre; the ruthenate of potash forms an orange-yellow solution in water. The *sesquioxide* is the most stable of the oxides of the metal; it is obtained in the anhydrous form by igniting the metal in a current of air. It is insoluble in the alkalies; but with acids it forms soluble salts which have a yellow colour. The alkalies precipitate the hydrated oxide ( $\text{Ru}_2\text{O}_3, 3 \text{HO}$ ) from these solutions as a bulky blackish-brown powder.

There are 3 chlorides of ruthenium,  $\text{RuCl}$ ,  $\text{Ru}_2\text{Cl}_3$ , and  $\text{RuCl}_2$ . The *sesquichloride* is obtained by dissolving the sesquioxide in hydrochloric acid: on evaporation it yields a greenish blue deliquescent mass, which is soluble in alcohol. Sulphuretted hydrogen causes a brown precipitate of sulphide of ruthenium in

solutions of the sesquichloride, leaving a supernatant liquid of a fine blue colour, probably owing to the formation of protochloride of the metal; this reaction is very delicate, and characteristic of ruthenium. Metallic zinc also reduces the yellow sesquichloride to the blue protochloride. *Formiate* or *oxalate of soda*, if boiled with salts of ruthenium, renders the solution colourless, but does not occasion any precipitate of reduced metal.

### VIII. OSMIUM

*Symbol*, Os; *Equivalent*, 99.41.

(841) OSMIUM may be obtained in the metallic condition by several processes. One of the simplest consists in treating osmic acid ( $\text{OsO}_4$ ) obtained by Fremy's method (839) with hydrochloric acid and metallic mercury. Calomel is thus produced by the decomposition of the suboxide of mercury, which is formed at the expense of the oxygen contained in the oxide of osmium;  $\text{OsO}_4 + 8 \text{Hg} + 4 \text{HCl} = \text{Os} + 4 (\text{Hg}_2\text{Cl}) + 4 \text{H}_2\text{O}$ . The water and the superfluous acid are expelled by evaporation to dryness, and on heating the residue in a small porcelain retort the excess of mercury and calomel are driven off, leaving pure osmium in a pulverulent form. In this finely divided state, it takes fire when heated in the open air, and is dissolved by strong nitric acid, or by aqua regia, being converted into osmic acid. After ignition, however, it is no longer soluble in the acids, and is neither volatile nor fusible. The specific gravity of osmium in the pulverulent form is about 10. It would no doubt be higher if it could be obtained in compact masses. The specific gravity of the alloy of osmium and iridium, which contains nearly half its weight of osmium, is about 21.

Osmium differs remarkably from the other metals of this group, and presents more analogy with arsenic and antimony than with the noble metals.

(842) Five *oxides of osmium* are known;— $\text{OsO}$ ,  $\text{Os}_2\text{O}_3$ ,  $\text{OsO}_2$ ,  $\text{OsO}_3$ ,  $\text{OsO}_4$ . The *protoxide* is of a dark green colour, it is soluble in acids, and forms green salts. The *sesquioxide* has not been isolated; it forms yellow uncrystallizable salts. The *binoxide* is black. The *teroxide* possesses the characters of a weak acid; it cannot be isolated, but it forms a crystalline compound with potash ( $\text{KO}$ ,  $\text{OsO}_3$ ,  $2 \text{HO}$ ) which is sparingly soluble. This compound furnishes a good source of pure osmium. It is easily obtained by the addition of a little alcohol to a solution of the per-



oxide of osmium in potash; the osmite separates in large rose-coloured octohedra, which are permanent in a dry air, but absorb oxygen if moist. *Osmic acid*,  $\text{OsO}_4$ , is the volatile compound which is produced when the metal is heated with nitre, or when roasted in air; it forms colourless, acicular, transparent, flexible crystals which are freely soluble in water; its vapour is irritating and deleterious, having a pungent odour somewhat resembling that of chlorine: hence the name of the metal osmium (from  $\sigma\sigma\mu\eta$ , 'odour'): it does not combine with acids; but though it unites with the alkalis, its solution does not redden litmus. It produces a permanent black stain upon the skin when touched, and gives a characteristic blue precipitate when its solutions are mixed with tincture of galls. If the solution of osmic acid be mixed with muriate of ammonia, a yellow sparingly soluble salt is formed ( $\text{H}_4\text{NCl}, \text{OsO}_2\text{H}_2\text{N}$ ), which, when ignited in a current of hydrogen, leaves pure osmium (Fremy).

If the aqueous solution of osmic acid be treated with sulphuretted hydrogen, an immediate precipitate of the black hydrated *quadrisulphide* occurs, which is slightly soluble in solutions of the alkaline sulphides. Four inferior degrees of sulphuration of osmium also exist; they correspond in composition with the oxides.

(843) There are 4 *chlorides of osmium*,  $\text{OsCl}$ ,  $\text{Os}_2\text{Cl}_3$ ,  $\text{OsCl}_2$ ,  $\text{OsCl}_3$ : the *protochloride* is green, and sublimes in green needles; it is produced by heating powdered osmium in a current of chlorine; the double salts which it forms are of a green colour. The *bichloride* is formed in the same way as the protochloride, by employing an excess of chlorine; it is more volatile, and condenses as a red, crystalline, fusible, deliquescent powder: both this and the preceding chloride are dissolved by water, which soon decomposes them, forming osmic and hydrochloric acids, and depositing metallic osmium. The bichloride forms, with chloride of potassium, a beautiful sparingly soluble red salt, which dissolves in water and furnishes octohedral crystals ( $\text{KCl}, \text{OsCl}_2$ ); this salt is obtained by heating a mixture of osmium with chloride of potassium in a current of chlorine: it is isomorphous with the corresponding platinum salt. Double salts may also be formed which contain both a sesquichloride and a terchloride of osmium.

A compound of nitrogen, oxygen, and osmium ( $\text{OsN}, \text{OsO}_4$ ), was formed by Fritzsche and Struve. It may be obtained by acting upon a mixture of caustic potash and ammonia by means of osmic acid; these chemists termed it *osman-osmic acid*. With the alka-

lies it forms yellow crystalline compounds, which detonate readily when they are struck or suddenly heated.

The properties of the salts of osmium have been but incompletely ascertained.

### §.IX. IRIDIUM.

*Symbol, Ir; Equivalent, 98.56.*

(844) IRIDIUM is occasionally found native and nearly pure in considerable masses among the Uralian ores of platinum, but it usually occurs combined with osmium as an alloy in flat scales. Iridium appears to be dimorphous, as it is found crystallized both in cubes and in double 6-sided pyramids (G. Rose). In order to obtain the metal in the separate state, Wöhler recommends the powdered alloy to be intimately mixed with an equal weight of finely powdered fused chloride of sodium, and the mixture to be heated to dull redness in a glass tube through which a current of dry chlorine is transmitted as long as it is absorbed. The alloy is decomposed by the chlorine; double chlorides of iridium and sodium, and of osmium and sodium are thus formed. They are dissolved in boiling water, and are thus freed from the insoluble portions. The solution is then concentrated, and the salt so obtained is mixed with nitric acid and distilled; the double salt of osmium is thus decomposed, and osmic acid is formed, whilst the iridium salt remains in the liquid: the osmic acid being volatile, is expelled during the distillation: the addition of muriate of ammonia to the concentrated solution in the retort produces a precipitate of the double chloride of iridium and ammonium, which, upon ignition, yields metallic iridium. The metal, however, if obtained thus, is liable to be contaminated with ruthenium. It is preferable to adopt Fremy's method of procuring the double chloride of iridium and potassium (839). This salt may be decomposed by ignition in a current of hydrogen; the chloride of potassium may be removed by washing with water, when the iridium is left in the form of a finely divided powder.

Iridium is a very hard, white, brittle metal, which is infusible except by the heat of the voltaic current. If heated in a finely divided form in the open air it absorbs oxygen, but if in mass it remains unchanged by exposure to heat. In its isolated form it is unacted on by any of the acids or by aqua regia, but when alloyed with platinum is readily dissolved by aqua regia. Pulverulent iri-

dium, when fused with nitre or with the alkalis, becomes oxidized, and a similar effect is produced by heating it with bisulphate of potash. Iridium may be obtained in a finely divided state by decomposing a solution of its sulphate by alcohol. It forms a black powder, which possesses properties similar to those of platinum black (823).

(845) *Oxides of Iridium*.—This metal forms three distinct combinations with oxygen,  $\text{IrO}$ ,  $\text{Ir}_2\text{O}_3$ , and  $\text{IrO}_2$ ; they pass readily one into the other, and thus give the variety of tints which solutions of its salts assume. From these changes of colour the name of iridium, derived from Iris, the rainbow, was conferred on the metal.

The *protoxide* is obtained as a black anhydrous powder by decomposing the dry protochloride by means of a concentrated solution of potash. It is attacked by acids with difficulty, but is dissolved by the alkalis; the solution in potash absorbs oxygen from the air, and becomes blue. Its solutions in the acids have a dingy green colour.

The *sesquioxide* is the compound formed when iridium is fused with potash or with nitre, or by heating the pulverulent metal in air. It is a bluish-black powder, which is decomposed by a full red heat, and is readily reduced by hydrogen and combustible substances. This anhydrous oxide is soluble in acids. If a solution of sesquichloride of iridium be boiled with solution of potash, oxygen is absorbed, and an indigo blue precipitate which is a hydrate of the *binoxide of iridium* ( $\text{IrO}_2, 2\text{HO}$ ) is formed (Claus). It may be rendered anhydrous by a gentle heat. It is but slowly dissolved by acids: the hydrochloric solution is at first blue, it then becomes green, and when heated, changes to reddish-brown, whilst bichloride of iridium is formed.

Three *sulphides* of iridium corresponding to the oxides may be prepared by decomposing the chlorides of the metal by means of sulphuretted hydrogen.

Iridium, like palladium, when held in the flame of a spirit-lamp, becomes covered with carbonaceous excrescences, which contain a considerable portion of metallic iridium.

(846) *Chlorides of Iridium*.—These correspond in number and composition with the oxides. They all form double salts with the alkali chlorides. The *sesquichloride* is the most stable of the three chlorides; it forms salts with chloride of sodium and with chloride of potassium. If dry chlorine be transmitted over a mixture of finely divided iridium and chloride of potassium, a double salt,

of a reddish-black colour ( $\text{KCl}$ ,  $\text{IrCl}_2$ ), consisting of bichloride of iridium and potassium, is formed. It may be dissolved in boiling water, and is deposited in octohedra on evaporating. It corresponds in composition to the platinum salt, with which it is isomorphous. A similar salt of sodium may be formed in the same manner, by substituting chloride of sodium for chloride of potassium: it is freely soluble. Bichloride of iridium forms a similar salt with sal-ammoniac, which possesses a very intense colouring power, and produces a dull brown solution even when much diluted. Bichloride of iridium, when heated with ammonia, forms a series of compound bases analogous to those furnished by platinum. M. Claus considers that the compounds formerly described as containing tetroxide and trichloride of iridium were really compounds of ruthenium.

The salts of iridium have been but incompletely examined.

## CHAPTER XVIII.

### ON SOME CIRCUMSTANCES WHICH MODIFY THE OPERATIONS OF CHEMICAL AFFINITY.

(847) IN the first part of this work an outline was given of the leading characters of the most important varieties of molecular and polar forces, as viewed in their simplest conditions. In the second portion of the work the attention of the reader has hitherto been directed principally to the results produced by the exertion of chemical affinity in the formation of the various compounds of inorganic origin, without reference to the effects of other forces which may have concurred in their production. It will, however, now be advisable to trace the influence exerted upon the operation of chemical affinity by the co-operation or antagonism of elasticity and cohesion, of adhesion, and of light, heat, and electricity. Cases in which the chemical decomposition of one substance by another is due simply to differences in the degree of chemical affinity are much less numerous than might at first be imagined. The displacement of one metal by another from its solutions, such as that of silver by mercury, of mercury by copper, of copper by lead, and of lead by zinc (7, 5), furnishes some of the best examples of this kind; and similar instances are afforded by the displacement of one base by another insoluble base, as when oxide

of copper is displaced from its combination with nitric acid by boiling it with freshly precipitated oxide of zinc, or oxide of silver.

§ 1. INFLUENCE OF COHESION, ADHESION, AND ELASTICITY.

(848) *Influence of Cohesion upon Affinity*.—Since chemical affinity is a molecular force, which is exerted only when the particles of bodies are within distances indefinitely small, minute subdivision, and diminution of cohesion, might be expected to favour its manifestation, by increasing the surfaces, and facilitating the mutual contact, of the combining bodies. It will therefore be needless to give more than one or two instances in proof of this point. Iron, copper, lead, and many other metals, when exposed to the atmosphere in mass, are acted upon very slowly by it, and they gradually become converted into oxide upon the surface: if, however, they be reduced to a finely divided state, they are oxidized with such rapidity as often to become incandescent. If iron, cobalt, or nickel be reduced by hydrogen from its oxide, at a low red heat, it is obtained in this form: by the interposition of some infusible matter between the particles of the precipitated oxide, such, for example, as a little alumina or magnesia, the tendency to rapid oxidation is much increased; probably because the cohesion of the fine particles of reduced metal is mechanically prevented, and the access of the air to each portion takes place with facility. Copper, when precipitated from its solutions by metallic iron, or when reduced by means of hydrogen from its oxide, at a low temperature, often takes fire and glows like tinder, when only a very slight elevation of temperature is applied to it. If a portion of tartrate of lead be exposed in a glass tube to a heat sufficient to char the acid, the metallic lead is reduced throughout the mass in a state of extreme division, and when poured into the air it generally takes fire, and burns with scintillations.

The opposite influence, exercised by the force of cohesion, is seen on contrasting the facility with which disintegrated carbon burns in the shape of tinder, with the difficulty which is experienced in effecting the combustion of the compact coke, which is deposited from coal gas upon the interior of the iron retorts; and a decrease of combustibility may be traced through all the different forms of carbon, in proportion as their hardness and density increase.

(849) *Influence of Adhesion and Solution on Affinity*.—It is mainly to the intimate subdivision effected by means of solution,

that its important influence in facilitating chemical combination is due. The force of cohesion amongst the component particles of the bodies dissolved is balanced by their adhesion to those of the liquid, and the particles of the substance in solution being free to move in any direction, easily obey the force of affinity.

The important influence of cohesion in preventing chemical action, and the manner in which the force of adhesion, as displayed in the production of solution, may act in favouring chemical action, are well exemplified by the action of nitric acid upon carbonate of baryta. Nitrate of baryta, although soluble in water and dilute nitric acid, is not soluble in the concentrated acid; when, therefore, concentrated nitric acid is poured upon finely powdered carbonate of baryta, it occasions but a slight effervescence, which speedily comes to an end, although the acid may be in large excess. If the liquid be diluted with a small quantity of water, a brisk effervescence is temporarily renewed, but again soon ceases; on a further addition of water, a fresh effervescence occurs, and when the acid has been diluted with 8 or 10 times its bulk of water, the whole of the carbonate of baryta is decomposed and dissolved.

For a similar reason, alcoholic solutions of acids are without action on the carbonates, unless the resulting salt be soluble in alcohol. A mixture of tartaric acid and alcohol will not decompose the carbonate of potash. Hydrochloric acid, dissolved in alcohol will not decompose carbonate of potash, but will decompose carbonate of lime. An alcoholic solution of nitric acid decomposes carbonate of lime, but not carbonate of potash. The tartrates are insoluble in alcohol, so are chloride of potassium and nitrate of potash, but chloride of calcium and nitrate of lime are solved by alcohol freely.

(850) *Influence of Elasticity.*—In the numerous instances in which two salts mutually decompose each other, frequent examples are afforded of the results produced by the interference of other forces with that of chemical affinity. The action of sulphate of ammonia and carbonate of lime is a case in point. If these two salts be mixed in a dry state, at ordinary temperatures, they do not appear to act upon each other; but if subjected to the influence of a gentle heat, a double decomposition occurs, carbonate of ammonia and sulphate of lime are produced; the volatile carbonate of ammonia is expelled, and by the aid of the force of elasticity, it is removed from the mixture;  $\text{CaO}$ ,  $\text{CO}_2 + \text{H}_4\text{NO}$ ,  $\text{SO}_3$  yielding  $\text{H}_4\text{NO}$ ,  $\text{CO}_2 + \text{CaO}$ ,  $\text{SO}_3$ . But suppose a solution of sulphate of lime to be mixed with one of carbonate of ammonia, the effects are

exactly reversed; carbonate of lime, owing to its insolubility and the predominance of cohesion among its particles, is precipitated, whilst the soluble sulphate of ammonia remains in the liquid; and now  $\text{H}_4\text{NO}$ ,  $\text{CO}_2 + \text{CaO}$ ,  $\text{SO}_3$  become  $\text{CaO}$ ,  $\text{CO}_2 + \text{H}_4\text{NO}$ ,  $\text{SO}_3$ . The chemist very often avails himself of the influence of elasticity in promoting chemical decomposition. When, for example, an acid is added to a salt, it may decompose that salt, and take the place of the acid previously in combination with the base, provided that the original acid can assume the gaseous form at ordinary temperatures, or can be converted into vapour, at a temperature below that required to volatilize the acid employed to displace it. Carbonic acid may thus be displaced from the carbonates by solutions of all the ordinary mineral and vegetable acids, except the hydrocyanic and hydrosulphuric acid.

It is upon this principle that sulphuric acid, when aided by heat, is employed to displace the nitric, the hydrochloric, the acetic, the formic, the butyric, and other volatile acids from their salts by distillation. Even a feebler but more fixed acid may expel the stronger acids which are more volatile than itself; thus, oxalic acid, if boiled with solutions of the chlorides, expels hydrochloric acid from the liquid with facility.

A remarkable illustration of the important influence exerted by elasticity in counteracting powerful chemical affinities, is afforded in the decomposition of the sulphates themselves, by weaker acids at a high temperature:—for example, the affinity of sulphuric acid for bases is of the most energetic kind, whilst that of boracic acid, on the contrary, is extremely feeble: if a solution of borax be mixed with sulphuric acid, the soda of the salt will enter into combination with the sulphuric acid as it is added, and will gradually be separated from the boracic acid, which, if the liquid be hot and not too concentrated, is retained in solution. Owing to the peculiar action of boracic acid on blue litmus, it can be shown that the two acids do not divide the soda between them, for if a piece of blue litmus paper be placed in the liquid, it will exhibit the peculiar wine-red tint due to boracic acid, until a quantity of sulphuric acid exactly equivalent to the soda contained in the borax has been added; but the moment that this point is reached, the least excess of sulphuric acid immediately reveals itself by the change of the colour of the litmus from dusky purplish-red to a bright red. It is therefore quite clear that boracic acid cannot effect even a partial displacement of sulphuric acid from its combination with soda when the two are in solution. But it is otherwise at a red heat:

if boracic acid be fused with sulphate of soda, borax is produced, and sulphuric acid, which is volatile at this high temperature, is expelled in the elastic form. Other acids which are known to have a feeble affinity for bases than sulphuric acid, but which support a red heat without experiencing volatilization, such as the phosphoric and silicic acids, are able to decompose the sulphates when heated with them.

In like manner, when a base which is fixed, is heated with the salt of a volatile base, the volatile base is displaced by the more fixed one; thus quick lime, or potash, if heated with the salts of ammonia, is converted into a salt of lime or of potash, whilst the ammonia escapes in the gaseous state.

(851) The effect of elasticity, in removing from the sphere of action one of the components of a body which is undergoing decomposition, may in some cases be considerably assisted by mechanical means; and when the affinities of the displacing body, and of the substance displaced by it for the other constituent of the compound, are nearly equal, effects which are in apparent opposition to each other may sometimes be produced. For instance, oxide of iron, when heated to redness in a current of hydrogen gas, is gradually reduced to the metallic state;—the steps of the process appear to be these: a small quantity of water is formed; it immediately diffuses itself in vapour into the hydrogen, and is mechanically carried away by the current of this gas, which must be employed in considerable excess for this purpose; and this process goes on until the reduction is complete. On the other hand, if metallic iron be heated in a current of steam, water is decomposed, hydrogen is liberated, and is carried beyond the reach of chemical action upon the iron by the excess of the steam employed. In a similar manner, if a current of sulphuretted hydrogen be transmitted in large excess over solid bicarbonate of potash, aided by a gentle heat, the whole of the carbonic acid and water will be displaced from the bicarbonate, and carried forward by the excess of the gas, whilst sulphide of potassium will be formed. But sulphide of potassium, if dissolved in water, and subjected to a current of carbonic acid, will, in its turn, be gradually but completely decomposed; the sulphuretted hydrogen being carried away by the excess of carbonic acid, whilst bicarbonate of potash is formed in the liquid.

(852) If elasticity be prevented by mechanical means from exerting its influence in removing a body from contact with others for which it has an affinity, combinations may be obtained, which



cannot otherwise be procured. Wöhler (Liebig's *Annalen*, lxxxv. 376) found that a hydrate of sulphuretted hydrogen may be obtained in colourless crystals, if a portion of persulphide of hydrogen, freed from acid, be sealed up in a strong glass tube, with a small quantity of water; the persulphide gradually undergoes decomposition into crystallized sulphur and gaseous sulphuretted hydrogen, which, at ordinary temperatures, exerts a pressure of about 17 atmospheres. Under these circumstances it combines with water, and forms a crystalline solid, which disappears with effervescence when the tube is heated to  $86^{\circ}$ , but is reproduced on cooling. If a tube, containing crystals of this compound, be opened, the crystals immediately disappear with brisk effervescence. In other cases, the decomposition of compounds already formed may be retarded or prevented, by preventing the escape of the elastic constituent by mechanical means. Hydrate of chlorine offers an instance of this kind. Under ordinary circumstances this substance becomes liquid at a few degrees above the freezing point of water, with escape of gaseous chlorine; but if the solid hydrate be sealed up in a glass tube it remains solid even when the temperature rises as high as  $70^{\circ}$ ; the pressure of chlorine within the tube retarding the decomposition. Again, carbonate of lime is decomposed in an open fire, at a red heat, into carbonic acid and quick lime, but if it be enclosed in an iron tube, the mouth of which is plugged to prevent the escape of the acid, the carbonate may be melted, and on cooling it furnishes a granular mass, which is still carbonate of lime, and has the appearance of marble.

(853) *Action of Acids on Salts in Solution.*—Whenever an acid is added to a salt with the base of which it is capable of forming a soluble compound, it may be supposed to produce a division of the base between itself and the acid with which it was previously united, so that two acids, and two salts may be present in the liquid, in some unknown proportions depending upon the strength of the relative affinities of the base for the two acids:—thus, when nitrate of potash is mixed with sulphuric acid, part of the potash may be supposed to enter into combination with the sulphuric acid, and part to remain united with the nitric acid, while a portion of nitric acid will be liberated, and will mix with the uncombined sulphuric acid: thus,  $2(\text{HO}, \text{SO}_3) + 2(\text{KO}, \text{NO}_5) = \text{KO}, \text{NO}_5 + \text{KO}, \text{SO}_3 + \text{HO}, \text{NO}_5 + \text{HO}, \text{SO}_3$ . The occurrence of such a decomposition as this, although probable, in many cases does not admit of direct proof. If an additional force be called

into operation, such as the development of elasticity on the application of heat, the more volatile acid may be expelled in the form of vapour, and may thus be withdrawn from the sphere of action. This, however, is no proof that such a partition of the base actually existed previous to the application of heat. In cases where the affinity of one acid for the base is very strong, whilst that of the other is feeble, the stronger acid may (as in the case of sulphuric acid and borax already cited) entirely appropriate the base to itself. But where the two acids at all approach each other in chemical power, it must be assumed that a division of the base takes place. Sometimes the occurrence of such a partition can be proved by the change of colour which ensues after the mixture has been effected. Sulphate of copper, for example, is of a blue colour when in solution, and chloride of copper is green. If a solution of the blue sulphate be mixed with hydrochloric acid, it is evident that the oxide of copper enters partially into combination with the hydrochloric acid, since the solution assumes a bright green tint;  $2(\text{CuO}, \text{SO}_3) + 2 \text{HCl} = \text{CuO}, \text{SO}_3 + \text{CuCl} + \text{HO}, \text{SO}_3 + \text{HCl}$ .

If the base form an insoluble compound with the newly added acid, it is possible to decompose the original salt completely by its means. Thus, if a solution of nitrate or of acetate of baryta be mixed with sulphuric acid, it may be supposed that the baryta divides itself between the two acids in proportion to its affinity for each; but the sulphate of baryta being insoluble, is at once withdrawn from the mixture, and the baryta remaining in the original salt again divides itself between the two acids: the fresh portion of sulphate of baryta, however, is immediately precipitated; and so, by a series of steps which, where the affinities are strong, succeed each other far more rapidly than they can be described,—the whole of the baryta is separated in the form of an insoluble sulphate, leaving the nitric or the acetic acid free in the solution.

A very feeble acid may even displace a more powerful one when the compound which it forms is insoluble in the menstruum in which it is suspended. Hydrocyanic acid will separate nitric acid from oxide of silver, owing to the formation of the insoluble cyanide of silver;  $\text{AgO}, \text{NO}_5 + \text{HCy} = \text{HO}, \text{NO}_5 + \text{AgCy}$ . Tartaric acid will liberate sulphuric acid in a solution of sulphate of silver, owing to the formation of an insoluble tartrate of silver. Oxalic acid will precipitate oxalate of copper from a solution of chloride of copper; and Pelouze has observed that, if a current of carbonic acid be transmitted through a solution of acetate of potash dissolved in alcohol, acetic acid will be liberated, and carbonate of

potash, which is insoluble in alcohol, will be separated; but no such change occurs in its aqueous solution, since carbonate of potash is freely soluble in water. This rule, however, is not without exception, where one acid is very powerful and the other is very feeble; borate of lime, for instance, is an insoluble salt, but a solution of boracic acid will not occasion any precipitate if mixed with one of nitrate of lime.

In like manner if the acid originally present be insoluble in water, it will be separated, and the salt will be decomposed; thus, on the addition of nitric acid to a solution of tungstate of potash, the tungstic acid is precipitated, whilst nitrate of potash is retained in the solution;  $\text{KO}, \text{WO}_3 + \text{HO}, \text{NO}_5 = \text{KO}, \text{NO}_5 + \text{HO}, \text{WO}_3$ .

(854) *Action of Bases on Salts in Solution.*—An analogous decomposition occurs if a quantity of some additional base be added to a saline solution. If the two bases be soluble, and the salts which they form be also soluble, the solution will remain clear, and it may be supposed that the acid is divided between the two bases in proportion to its affinity for each, as when a solution of nitrate of baryta is mixed with a solution of potash: a mixture of nitrate of baryta and nitrate of potash with free baryta and free potash is thus obtained; but as baryta is less soluble than potash, a portion of the baryta will gradually be deposited if the solutions be in a concentrated form. If either of the bases be insoluble, or form an insoluble salt with the acid, a complete separation of the base or of the acid contained in the original salt may be effected. For example, the salts of nearly all the metals, with the exception of those of the alkalies and of the alkaline earths, contain as bases metallic oxides which are not soluble in water: the addition of any soluble base, such as potash, soda, or ammonia to their solutions, immediately occasions the precipitation of the insoluble oxide. It is in this manner that such oxides are commonly prepared from their solutions: for example, the oxide of zinc, of iron, of cobalt, of nickel, of manganese, or of silver is thus completely separated from the acid by which it was previously held in solution; thus,  $\text{CoO}, \text{SO}_3 + \text{KO}, \text{HO} = \text{CoO}, \text{HO} + \text{KO}, \text{SO}_3$ . Solution of baryta, of strontia, or of lime, would act in a similar manner, if the acid, like the nitric or the hydrochloric, were capable of forming a soluble compound with these bases. Nitrate of copper might thus be decomposed by a solution of baryta;  $\text{CuO}, \text{NO}_5 + \text{BaO}, \text{HO} = \text{BaO}, \text{NO}_5 + \text{CuO}, \text{HO}$ .

In a few cases no precipitation occurs even though the oxide be insoluble; thus, when cyanide of mercury is mixed with

a solution of potash, no precipitate is produced, although oxide of mercury is insoluble in water.

If the newly added base form an insoluble compound with the acid, it is wholly precipitated by it; and if the other base be soluble, it remains in the liquid. One of the methods of forming a pure solution of potash is founded on this principle; in this experiment a solution of sulphate of potash is mixed with a quantity of solution of baryta exactly sufficient to precipitate the whole of the sulphuric acid;  $\text{KO}, \text{SO}_3 + \text{BaO}, \text{HO} = \text{K}_2\text{O}, \text{HO} + \text{BaO}, \text{SO}_3$ : and in a similar manner oxalate of potash is deprived of its oxalic acid by the addition of lime-water to its solution, owing to the formation of an insoluble oxalate of lime. If the base as well as the salt which is formed by the addition of the new base to the acid be insoluble, it is possible to precipitate the whole of both acid and base from the liquid simultaneously; as when a solution of baryta is added in regulated quantities to a solution of sulphate of silver;  $\text{AgO}, \text{SO}_3 + \text{BaO}, \text{HO} = \text{Ag}_2\text{O}, \text{HO} + \text{BaO}, \text{SO}_3$ .

(855) *Mutual Action of Salts in Solution.*—It is a rule almost without exception,\* that when solutions of two salts, capable of forming by mutual interchange of acids and bases an insoluble or sparingly soluble salt, are mixed, the salts decompose each other, and the compound which is least soluble is precipitated. It is in this manner that the greater number of insoluble compounds are formed by the process of double decomposition. Chloride of silver is thus obtained by acting upon solution of nitrate of silver with one of common salt;  $\text{AgO}, \text{NO}_5 + \text{NaCl} = \text{NaO}, \text{NO}_5 + \text{AgCl}$ : and in a similar manner, if carbonate of manganese or phosphate of copper be required, it may be procured by mixing a solution of chloride of manganese or of sulphate of copper with one of carbonate of potash or of phosphate of soda. Sometimes a soluble compound may advantageously be procured in this manner, as in the ordinary method of preparing acetate of alumina, in which a solution of acetate of lead is mixed with one of sulphate of alumina: sulphate of lead is precipitated, and acetate of alumina remains dissolved;  $3(\text{PbO}, \text{C}_4\text{H}_3\text{O}_3) + \text{Al}_2\text{O}_3, 3 \text{SO}_3 = 3(\text{PbO}, \text{SO}_3) + \text{Al}_2\text{O}_3, 3(\text{C}_4\text{H}_3\text{O}_3)$ .

When two saline solutions are mixed, which form, by the mutual interchange of their acids and bases, salts which are also

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\* When solution of cyanide of mercury is mixed with one of nitrate of silver little or no precipitate is produced, although cyanide of silver is a very insoluble compound, and cyanide of mercury has not the power of forming a soluble double cyanide with it.

freely soluble, in ordinary cases there is no proof that any change occurs, but it is usually supposed that a mixture of four different salts is produced. When, for instance, solutions of sulphate of potash and nitrate of soda are mingled, it is imagined that a mixture of sulphate of potash and sulphate of soda, of nitrate of potash and nitrate of soda, in unknown proportion, dependent upon the balance of the mutual affinities of the acids and bases, is the result. In like manner the mixture of three different acids and three different bases would occasion the formation of nine different salts; and the mixture of four salts, each containing different acids and different bases, should produce sixteen different salts, provided that all are capable of coexisting in solution.

Hence it will be seen that it is impossible to state with certainty what are the salts which are present in mixture in any solution which contains a number of saline compounds. In the analysis of a mineral water, for example, it is possible to determine the amount of each acid and of each base which is present, but it is not possible to say what the salts really were which were brought into solution to form the mineral water in question. Sulphuric acid, nitric acid, carbonic acid, and chlorine may have been present amongst the acid constituents, and potash, soda, lime, and magnesia amongst the bases: but it is impossible to say how all those acids and bases are distributed in the solution. Many chemists allot the bases to the acids in the order of the insolubility of the different salts, whilst others allot the strongest bases to the strongest acids. In reporting the results of analysis, however, the quantities of the separate acids and bases should invariably be given, in addition to which, the analyst, if he pleases, can allot them according to his fancy. The foregoing remarks may be illustrated by the curious alternate decompositions which differences of solubility at different temperatures sometimes bring about; a striking instance of this kind occurs in the case of a mixture containing both sulphate of magnesia and common salt. These salts occur mixed together on a large scale in the mother liquor of sea-water, after the bay-salt has been separated. Four salts may be formed by the intermixture of these two compounds, viz., sulphate of magnesia, sulphate of soda, chloride of magnesium, and chloride of sodium. Of these four salts chloride of sodium is the least soluble at the boiling point; if, therefore, the solution be concentrated by ebullition, chloride of sodium is separated in crystals; and as the liquid cools, the sulphate of magnesia crystallizes out. The effect, however, will be different if the solution

be allowed to evaporate spontaneously in the open air; at low temperatures the sulphate of soda is the least soluble of the four salts; and at low temperatures it is the sulphate of soda which separates in crystals from the liquid, whilst the readily soluble chloride of magnesium remains in solution.

Upon a similar principle nitrate of soda is converted on a large scale into nitrate of potash, by mixing it with chloride of potassium; on concentrating the solution by boiling it, chloride of sodium is separated in crystals, and nitrate of potash crystallizes out as the liquid cools: at low temperatures chloride of sodium is more soluble than nitrate of potash, and the nitre crystallizes out nearly in a state of purity.

It may, in fact, be stated as a general principle, that on concentrating a mixed solution by evaporation, the salt which is least soluble at that particular temperature is that which is first formed.

In certain cases where there is no great difference in the solubility of two salts, evidence is afforded of their mutual decomposition when the solutions are mixed, by the change of colour which then ensues. Sulphocyanide of potassium, for example, when mixed with a solution of perchloride of iron, so much diluted as to be colourless, indicates by the blood-red solution which it forms, that a mutual interchange of the components of the two salts has been partially effected. In like manner, when a solution of proto-sulphate of iron is mixed with one of acetate of soda, a brown colour, similar to that of the acetate of iron, is produced; and further, on transmitting a current of sulphuretted hydrogen through the liquid, the iron is precipitated in the form of a black sulphide. This reaction could only take place, owing to the presence of acetate of iron, since a solution of acetate of iron admits of being thus decomposed by sulphuretted hydrogen, but one of sulphate of iron is not so acted upon. The entire quantity of iron may be separated in this manner, as no sooner is a certain proportion of iron rendered insoluble, than a fresh portion of acetate of iron is formed; and this formation and decomposition of the salt continues as long as any iron remains in a state of solution.

(856) *Influence of Mass in the Formation of Chemical Compounds.*—A curious question presents itself as to the proportion in which two bodies are capable of thus mutually decomposing each other on mixture. When, for example, three different bodies, A, B, and C, are mixed together, one of which, C, is capable of combining with either of the other two, and forming with them compounds, A C, B C, which in both cases are soluble, the quantity of A and of B being

considerably in excess of  $c$ , will the proportion in which  $c$  enters into combination with  $A$  and  $B$ , be determined merely by the strength of their relative affinities? or, will the proportion in which each of these bodies is present, also influence the result? It was argued by Berthollet, that not only would  $c$  be divided between  $A$  and  $B$ , but that in proportion as the quantity of one of these bodies  $A$ , preponderated over the other body  $B$ , the proportion of  $A c$  in the mixture would be increased, while of course that of  $B c$  would be diminished. If, on the other hand, the proportion of  $B$  were increased, the quantity of the compound  $B c$  would be augmented, whilst that of  $A c$  would be proportionately lessened, the body  $c$  dividing itself between  $A$  and  $B$ , in a proportion represented by the product of its affinity for each of these elements multiplied into their mass. Thus if  $a$  represent the mass of  $A$ ,  $x$ , represent its affinity for  $c$ , if  $\beta$  be the mass of  $B$ , and  $y$  its affinity for  $c$ ;  $A c : B c :: ax : \beta y$ . Suppose, for example, a solution of nitrate of potash to be mixed with more than its equivalent of sulphuric acid; it is generally conceded that the potash divides itself between the two acids, forming a mixture of sulphate and nitrate of potash, with free sulphuric and nitric acids. Now if the quantity of sulphuric acid be increased, will the quantity of sulphate of potash which is formed be influenced by the amount of sulphuric acid which is thus added in excess? and if so, to what extent will this influence of the mass of the acid modify the simple effect of chemical affinity?

Let us imagine for example, that  $x$ , the affinity of sulphuric acid for potash = 5, whilst  $y$ , that of nitric acid for potash = 4. When an equivalent of sulphuric acid is presented to an equivalent of nitrate of potash, the mass  $a$  of sulphuric acid = 1 : that of the nitric acid  $\beta$  = 1 also.  $ax : \beta y$  as 5 : 4. The nitrate will be partially decomposed;  $\frac{5}{9}$  of the potash will enter into combination with the sulphuric acid, whilst  $\frac{4}{9}$  will be united with the nitric, and we shall have in the solution  $\frac{5}{9}$  (KO, SO<sub>3</sub>),  $\frac{4}{9}$  (KO, NO<sub>3</sub>),  $\frac{4}{9}$  (HO, SO<sub>3</sub>) and  $\frac{5}{9}$  (HO, NO<sub>3</sub>). But suppose, instead of adding 1 equivalent of sulphuric acid, 2 equivalents be employed, whilst the proportion of the nitrate remains unaltered; the mass  $a$  of the sulphuric acid is now 2, and  $ax : \beta y$  as 10 : 4. The proportion of nitrate of potash will be diminished, and there will be  $\frac{10}{14}$  (KO, SO<sub>3</sub>),  $\frac{4}{14}$  (KO, NO<sub>3</sub>),  $\frac{4}{14}$  (HO, SO<sub>3</sub>) and  $\frac{10}{14}$  (HO, NO<sub>3</sub>); and if 3 equivalents of sulphuric acid be employed to 1 of nitrate of potash, since the mass  $a$  of sulphuric acid is now = 3;  $ax : \beta y$  as 15 : 4; consequently the proportions of the ingredients would be  $\frac{15}{19}$  (KO, SO<sub>3</sub>),  $\frac{4}{19}$  (KO, NO<sub>3</sub>),  $\frac{4}{19}$  (HO, SO<sub>3</sub>), and  $\frac{15}{19}$  (HO, NO<sub>3</sub>); the

proportion of sulphate of potash continuing to increase, though in a decreasing ratio, for every addition of free sulphuric acid to the solution.

(857) No experimental solution of this problem was given by Berthollet, and the question fell into abeyance; but within the last few years several attempts have been made with considerable success to determine this question quantitatively. Dr. Gladstone (*Phil. Trans.* 1855, p. 179) has published a series of experiments in which he has made use of the change of colour which solutions of certain salts undergo on mixture with each other, as a means of ascertaining the extent to which this mutual decomposition proceeds when all the products remain in solution. The principle of his experiments will be easily understood. Solutions of several persalts of iron, such as the persulphate, the pernitrates, perchloride, peracetate, percitrate, &c., were prepared in such a manner that each should contain the same proportion of the sesquioxide dissolved in the same bulk of water (each of the solutions employed contained very nearly 1 grain of sesquioxide of iron in 1000 grain measures of water). A solution of pure sulphocyanide of potassium was then prepared of such a strength that when 1 measure of this solution and 4 of that of the iron salts were mingled, the proportion of sulphocyanogen should be exactly sufficient to convert the whole of the iron into persulphocyanide, if complete mutual decomposition occurred: thus the proportions of the two salts employed were such that it would be possible for exact mutual interchange to occur as represented in the following equation:  $\text{Fe}_2\text{O}_3, 3 \text{ NO}_5 + 3 (\text{K, Scy}) = \text{Fc}_2 \text{ Scy}_3 + 3 (\text{KO, NO}_5)$ . On making the experiment in this manner, it was found that the iron was never wholly converted into the red salt, for the tint was deepened by the addition of more either of the iron salt or of the sulphocyanide. In order to obtain a quantitative estimate of the amount of these effects, definite measures of the solution of pernitrates of iron and of sulphocyanide of potassium were mixed together, and the liquid so obtained was diluted with water until it occupied a known, but arbitrary volume. This diluted mixture furnished a liquid of a certain depth of colour which was employed as a standard of comparison. Another measure of the solution of pernitrates of iron, equal to that used in the standard solution, was mixed with regulated additions of the sulphocyanide of potassium, and the liquid thus obtained was diluted with measured quantities of water after each addition of sulphocyanide, until, as far as the eye could distinguish, this solution had the same depth of tint



as that employed as the standard; it was then assumed that the quantity of sulphocyanide of iron formed was proportionate to the bulk of the two solutions.\* Suppose that the standard solution occupied a volume of 880 measures. It was found that if twice the quantity of the sulphocyanide of potassium employed in the standard liquid were made use of in the new solution, this mixture would require dilution till it occupied 1270 measures. The proportion of sulphocyanide of iron formed in these two cases, was assumed to be as 880 to 1270, or as 1 to 1.44. The excess of sulphocyanide thus employed, had therefore withdrawn an additional quantity of iron from its combination with the nitric acid.

In this manner experiments were made with quantities of the sulphocyanide of potassium progressively increasing from  $\frac{1}{2}$  equivalent of the sulphocyanide to each equivalent of nitrate of iron, up to 375 equivalents of sulphocyanide to 1 equivalent of nitrate of iron, and it was found that the quantity of sulphocyanide of iron which was formed, continued to increase with every addition of sulphocyanide of potassium, though the effect of each consecutive addition became less and less marked.

It was ascertained, as indeed it was to be expected, that the proportions of sulphocyanide of iron, which are formed by the mixture of equivalent quantities of other salts of iron with given amounts of the sulphocyanide of potassium, vary with the nature of the acid in combination with the peroxide of iron. For example, it was found that when nitrate of iron was mixed with sulphocyanide of potassium, in the proportion of equivalent quantities of each, that 0.194 of an equivalent of the red salt was formed. When an equivalent of sesquichloride of iron was used, 0.173 of an equivalent was formed; when the sulphate was employed, 0.126 of an equivalent was produced; with acetate of iron 0.04 only was formed, and when citrate of iron was employed, the quantity of sulphocyanide of iron which it yielded was too small to admit of being estimated. The oxide of iron therefore retained these different acids with degrees of force which vary inversely with the quantity of sulphocyanide which is formed, whilst the potassium in the sulphocyanide attracted them with a power in direct proportion to these quantities. Various attempts have been made to obtain relative numerical expressions for the force of affinity by

\* Dr. Gladstone found that simple dilution of the sulphocyanide of iron reduced the tint in a proportion greater than could be accounted for by mere dilution, but this source of error was eliminated, and was not found to present itself in other cases, which he employed to test the accuracy of the general conclusion.

which different compounds are united, but they have all hitherto failed. Experiments conducted upon the principle of those of Gladstone appear to offer the fairest prospect of solving this interesting and important problem.

Besides the sulphocyanide of iron, Dr. Gladstone examined a variety of other coloured compounds; one of these was the scarlet bromide of gold, which becomes yellow when mixed with chlorides of potassium and sodium, to an extent varying with the proportion in which these salts are added: the sulphate of quinine, when mixed with a soluble chloride, iodide, or bromide, also afforded similar indications, as it loses its *fluorescent* character (or power of altering the refrangibility of the rays of light (104)) in proportion to the quantity of chloride or bromide with which it is mixed. From these and from a variety of other experiments, it appears that when two or more compounds in solution are made to act upon each other, provided that the products which they form by their mutual action are also soluble, the following conclusions may be drawn:—1. That mutual interchange between the bodies which are mixed takes place in determinate proportions. 2. That these proportions are independent of the manner in which the compounds were originally combined: thus, if sulphate of potash and pernitrate of iron be mixed in equivalent quantities, the result is the same as if nitrate of potash and persulphate of iron had been employed in equivalent quantities. This is a fundamental point in these inquiries, but if Dr. Struwe's observations, (quoted by Graham, *Elem. Chem.* 2nd Ed. p. 232) be correct,—viz., that in the preparation of mineral waters, the taste of the liquid varies, not only according to the nature of the salts, but also according to the order in which they are added,—it cannot be a general law. 3. That these proportions are dependent partly upon the strength of the mutual affinities of the components for each other, and partly also upon the *mass*, or relative proportion of each compound which is present in the mixture. 4. That the alteration of the mass of any one of these compounds alters the amount of all the other compounds which co-exist in the mixture in a regularly progressive ratio; and these quantities admit of being represented by regular curves. In most cases this adjustment of the relative quantities of the different bodies takes place immediately that the mixture is made.

(858) The results are different if the products of the chemical combination be at once removed from the sphere of action, as by the formation of gaseous compounds, or of an insoluble precipitate when two liquids are mixed. Bunsen has investigated the results

obtained in some cases of this nature. He found that when a mixture of hydrogen and carbonic oxide was detonated with oxygen in quantity insufficient for its complete combustion, the oxygen divided itself between the two gases in such a manner that the quantities of water and of carbonic acid produced were in very simple atomic relations to each other (*Liebig's Ann.*, lxxxv. 137). He exploded together mixtures of oxygen, hydrogen, and carbonic oxide, in varying proportions, the hydrogen and carbonic oxide being each in considerable excess over the oxygen: under such circumstances water and carbonic acid were formed; but the quantity of carbonic acid was greater, in proportion as the carbonic oxide preponderated, according to a certain law. Similar results were obtained by detonating cyanogen with a quantity of oxygen insufficient for its complete combustion; in such case nitrogen and a mixture of carbonic acid and carbonic oxide in simple proportions were obtained: and when a mixture of carbonic acid and hydrogen was detonated with a quantity of oxygen insufficient for the consumption of the hydrogen, a certain proportion of the carbonic acid was reduced to carbonic oxide, according to the terms of the same law.

The following is the law deducible from Bunsen's experiments:—1. When two gaseous bodies, A, B, are mixed with a third body, C, and fired by means of the electric spark, the body C takes from A and B quantities which always stand to one another in a simple atomic relation: so that for 1 atom of A C, 1, 2, 3, or 4 atoms of B C are produced; for 2 atoms of A C, 3, or 5, or 7 atoms of B C are formed. If one atom of the compound A C, and one of B C be formed in this manner, the mass of A may be increased in the presence of B, up to a certain point, without any change in that atomic proportion; but if a certain limit be passed, the relation of the atoms, instead of being as 1 : 1, suddenly becomes as 1 : 2, or as 1 : 3, or as 2 : 3; and so on.

2. When a body, A, acting upon an excess of any compound, B C, reduces it, so that A C is formed and B is set at liberty; then if B in its turn can reduce the newly-formed compound, A C, the final result is that the reduced part of A C is in simple atomic proportion to the unreduced part. In the case of these reductions also, the mass of one of the ingredients of the mixture may be increased up to a certain point without altering the relative proportions of the compounds obtained; but if increased beyond this limit a sudden alteration in the relative proportions of the products occurs; but these proportions still admit of being represented by simple ratios.

The following experiments illustrate the first part of the foregoing law :—On exploding mixtures of carbonic oxide and hydrogen, in the following proportions, Bunsen found that the quantities of carbonic oxide and hydrogen which were oxidized were in the proportions stated below :—

	Mixture detonated.			Ratio of Gases burned.	
	Oxygen.	Hydrogen.	Carb. Oxide.	Hydrogen.	Carb. Oxid.
I. . . .	10 . .	20 . .	79.4 . .	1 . .	2 . .
II. . . .	10 . .	20 . .	44.4 . .	2 . .	2 . .
III. . . .	10 . .	20 . .	12.1 . .	6 . .	2 . .
IV. . . .	10 . .	37 . .	31.5 . .	8 . .	2 . .

These experiments show that, as the proportion of carbonic oxide to the hydrogen in the mixture decreased, the proportion oxidized on detonation decreased also, but it decreased *per saltum*, not gradually, and these proportions were found to be uniformly the same on repeating the detonation with the same mixture, although the degree of compression to which the mixture was subjected during the detonation was considerably varied in different experiments.

The following are Bunsen's principal experiments in support of the second part of the foregoing law :—When carbonic acid is driven over ignited charcoal, it is wholly converted into carbonic oxide ; but when steam is transmitted over ignited charcoal, a mixture of hydrogen, carbonic oxide, and carbonic acid is produced, in the proportion of 4 volumes of hydrogen, 2 volumes of carbonic oxide, and 1 of carbonic acid. Again, when a mixture of cyanogen with atmospheric air and oxygen was detonated in the eudiometer in the proportion of 6.2 of cyanogen to 10 of oxygen,\* the cyanogen yielded 3 volumes of nitrogen, 2 of carbonic oxide, and 4 of carbonic acid : and when a mixture of 4.07 of carbonic acid, 33.25 of hydrogen, and 10 of oxygen was detonated, a portion of the carbonic acid yielded oxygen to the hydrogen, and was reduced to the state of carbonic oxide ; 3 volumes of carbonic oxide being formed whilst exactly 2 volumes of carbonic acid remained unacted upon, although a large excess of hydrogen was present.

M. Debus arrived at substantially the same results as those indicated by Bunsen for gaseous mixtures, by precipitating a mixture of lime and baryta water, by small proportions of solution

\* Cyanogen requires for the complete combustion of its carbon twice its volume of oxygen, so that 6.2 of cyanogen would have required 12.4 instead of 10 of oxygen ; there is therefore more oxygen than would suffice for the conversion of the carbon into carbonic oxide.

of carbonic acid, and by similar experiments upon a large excess of a dilute solution of the mixed chlorides of calcium and of barium to which a dilute solution of carbonate of soda was added.

In the experiments of Bunsen, it must be recollected that the first products of the chemical combination are immediately removed from the sphere of action: carbonic acid, and carbonic oxide, and water will not mutually react upon each other; and in the experiments of Debus, the carbonates of the earths being insoluble, are at once withdrawn from further action upon the mixture.

(859) *Adhesion*.—The influence of adhesion in aiding chemical action is often exerted by overcoming the opposite force of elasticity; this is exemplified by the manner in which water frequently favours the mutual action of dry gases upon each other. When, for example, dry sulphurous acid and dry peroxide of nitrogen are mixed together, no combination takes place between them; the addition of a few drops of water, however, causes them immediately to condense and to form the white crystalline compound which has been spoken of when treating of the manufacture of sulphuric acid (344, and note p. 568). If the elasticity of these gases be overcome by other means—if, for instance, they be liquefied by exposing them to a low temperature, combination occurs without the intervention of moisture. In like manner, sulphurous acid and sulphuretted hydrogen may be mixed when dry, without acting upon each other, but if water be present, the mutual decomposition of the two gases is the result.

Water, by overcoming the self-repulsion of the gases, favours their chemical action upon solid bodies. Hydrochloric acid, and ammonia, in their gaseous form, exert but little influence upon the metals or upon their salts, although when in solution their action upon them is rapid and powerful.

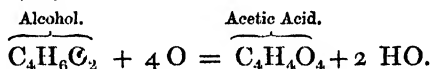
*Surface Actions*.—The adhesion of gases to solids produces many curious phenomena:—for example, let a piece of charcoal be thoroughly saturated with hydrogen by attaching it to the negative wire of the voltaic battery, and employing it as the platinode in the decomposition of acidulated water: this charcoal, if now detached from the battery and thrown into a solution of sulphate of copper, or of nitrate of silver, will effect the decomposition of these salts, and their respective metals will be thrown down upon the charcoal in the reduced state; the charcoal and condensed hydrogen appearing to act the part of a voltaic circuit, in which the hydrogen supplies the place of the electro-positive or oxidizable metal, and the charcoal that of the electro negative metal or conducting

plate. If a plate of platinum, rendered chemically clean,\* be introduced into a mixture of pure oxygen and hydrogen, in the proportions to form water, the gases become condensed upon the surface of the plate, and, being brought within the sphere of each other's attraction, begin to unite; at first slowly, but during the act of combination, heat is extricated, and the action proceeds more quickly, until at last the plate becomes red-hot, and an explosion of the gas ensues (*Faraday, Phil. Trans.*, 1834, p. 55). By employing the metal in a disintegrated or spongy form, the surface exposed is greater, and the action much more rapid: the metal conducts away but little of the heat which is generated, and soon becomes red-hot; whilst in the condition of platinum black (823) this activity attains its maximum. On throwing a little of this black powder into a mixture of oxygen and hydrogen it immediately becomes incandescent, and the gases combine with a loud report.

From its inalterability by ordinary chemical agents, platinum in this finely divided form has been used to effect various combinations which cannot otherwise readily be procured between vaporized and gaseous bodies:—For instance, if ammonia be mixed with atmospheric air, and transmitted over spongy platinum gently heated, its nitrogen becomes converted into nitric acid, and its hydrogen into water;  $\text{H}_3\text{N} + 8 \text{O} = 3 \text{H}_2\text{O} + \text{NO}_5$ ; but this transformation cannot be effected by heat, unless some substance analogous to spongy platinum be used, since nitric acid is decomposed at a temperature which, under ordinary circumstances, is required to effect the combustion of ammonia. On the other hand, ammonia may be formed from the oxides of nitrogen, by mixing them with hydrogen and transmitting the gases over platinum sponge gently heated;  $\text{NO}_2 + 5 \text{H} = \text{H}_3\text{N} + 2 \text{HO}$ . Nitrate of ammonia, when heated with platinum black, yields nitric acid, nitrogen, and water, instead of protoxide of nitrogen; thus  $5 (\text{H}_4\text{NO}_5) = 2 \text{NO}_5 + 8 \text{N} + 20 \text{HO}$ . A variety of other interesting changes may be effected. According to Döbereiner, (who first pointed out the remarkable power

\* This may be effected by holding the plate over the flame of a spirit lamp and rubbing it when hot, with a stick of caustic potash; the potash is to be maintained in a fused state upon its surface for a second or two; the alkali is then to be washed off completely in distilled water, and the plate is to be immersed for a minute in hot oil of vitriol; after which it is to be freed from adhering acid by immersion for a quarter of an hour in a large bulk of distilled

which finely divided platinum possesses of effecting these kind of combinations,) a mixture of cyanogen and hydrogen by the aid of a gentle heat yields cyanide of ammonium when in contact with spongy platinum. In a mixture of binoxide of nitrogen and olefiant gas, carbonate of ammonia is produced; and in a mixture of the vapour of alcohol and binoxide of nitrogen, cyanide of ammonium, carbonate of ammonia, olefiant gas, water, and a deposit of carbon are formed. In like manner, sulphurous acid may be rapidly converted into sulphuric acid, if it be driven in a moist state, mingled with air, through tubes containing spongy platinum: this method was even proposed as a manufacturing process for obtaining oil of vitriol, but it was abandoned in consequence of an alteration in the platinum, by which it is deprived of this power of effecting combination. Platinum black produces with the vapours of alcohol in contact with atmospheric air, a series of compounds which are finally converted into acetic acid (62).



For the success of these experiments, it is necessary that the surface of the platinum be chemically clean, otherwise the supposed adhesion of the gases or vapours to the metal does not take place. Faraday considers that these actions are owing to the adhesion of the gases to the surface of the metal, by which the particles of each gas are brought within chemical contact with the others. He observed that the admixture of small quantities of carbonic oxide, or of the vapour of bisulphide of carbon, or of olefiant gas\*, prevented the platinum from effecting the combination of the oxygen and hydrogen, but did not deprive the metal of its activity, as was ascertained by afterwards plunging it into a mixture of pure oxygen and hydrogen. On the other hand, the addition of sulphuretted or of phosphuretted hydrogen to an explosive mixture of oxygen and hydrogen, not only prevented the combination from being produced by the platinum, but it effected such an alteration of the surface of this metal that when it was plunged into a fresh portion of mixed oxygen and hydrogen, no combination of the gases occurred. Hydrochloric acid also rapidly destroys the peculiar properties of finely divided platinum. According to Döbereiner, the

\* Mr. Graham finds, that in the case of carbonic oxide, a gradual oxidation of the carbonic oxide takes place, but that this action is much slower than the oxidation of the hydrogen; the oxidizing influence is wholly concentrated on the carbonic oxide, and until this gas is entirely oxidated the hydrogen remains unaltered in the mixture.

Preventive action of this gas depends upon the decomposition of the hydrochloric acid by the oxygen condensed upon the platinum: water is formed whilst chlorine is liberated, and this chlorine, by converting the platinum superficially into protochloride, destroys its power; its activity, however, can be restored by treating it with boiling oil of vitriol. Hydrochloric acid is in this case expelled, and a small quantity of protoxide of platinum is dissolved; the metal is then to be well washed in distilled water.

(860) Other finely divided substances besides platinum possess this property of favouring the combination of oxygen and hydrogen in an inferior degree; even pounded glass, porcelain, charcoal, pumice, and rock crystal, if warmed to 600° F., produce this effect. Finely divided palladium, rhodium, and iridium also determine the combination of oxygen and hydrogen with explosion at ordinary temperatures. Gold and silver effect the combination of hydrogen with oxygen quietly, at temperatures far below the boiling point of mercury (Dulong and Thénard). Metals which have a strong affinity for oxygen cannot be used, as they immediately become oxidized upon the surface.

(861) *Catalysis*.—The remarkable actions produced by the agency of finely divided platinum have in the foregoing paragraphs been attributed to the force of adhesion, which is supposed to bring the different gaseous bodies within the sphere of mutual action; but they were viewed by Berzelius as arising from a new force, which he termed *catalysis*, in virtue of which, he says:—‘Certain bodies exert, by their contact with others, such an influence upon these bodies, that chemical action is excited; compounds are destroyed, or new ones are formed, although the substance by which these actions are induced does not take the slightest part in these changes.’ This catalytic force, however, is probably purely imaginary; most of the phenomena which have hitherto been referred to its agency being occasioned by several different causes, which often admit of being distinguished from each other, and which may, as in the case of the action of platinum, be explained by the active operation of other known forces.

One class of these phenomena are those included under the term *fermentation*. They are peculiar to the products of organic chemistry; such, for instance, as the change of solution of sugar into alcohol and carbonic acid, under the influence of *yeast*: the change of starch into sugar in the operation of mashing wort, or the germination of seeds, owing to the presence of a peculiar albuminous substance termed *diastase*: and the gradual conversion of amygdalin, the bitter principle in the bitter almond, into hydrocyanic



acid, oil of bitter almonds, sugar, and formic acid, when it is dissolved into water, and mixed with the *emulsin*, or albuminous principle contained in the pulp of the seed. In all these cases, however, although the constituents of the yeast, the diastase, or the emulsin, do not enter into the formation of the new products, yet they disappear during the change, and during the whole time are undergoing a series of specific alterations, which stand in intimate but unexplained relation to the metamorphosis of the sugar, the starch, or the amygdalin. One of the most remarkable features of these decompositions, is the small proportion of the ferment, or *catalytic body* as Berzelius would term it, which is required to produce the change: 1 part of yeast, for instance, is sufficient to convert 100 parts of sugar into alcohol and carbonic acid; and a still smaller quantity is required in the case of diastase, 1 part of which is able to effect the transformation of more than 1000 times its weight of starch into sugar. The consideration of these remarkable metamorphoses must however be deferred until the organic bodies themselves have been described.

Liebig's theory of catalysis is, 'that a body in the act of combination or decomposition, enables another body, with which it is in contact, to enter into the same state. It is evident,' says he, 'that the active state of the atoms of one body has an influence upon the atoms of a body in contact with it, and if these atoms be capable of the same change as the former, they likewise undergo that change, and combinations and decompositions are the consequence. \* \* \* This influence exerted by one compound upon the other, is exactly similar to that which a body in the act of combustion exercises upon a combustible body in its vicinity; with this difference only, that the causes which determine the participation and duration of these conditions are different.'

These explanations are hardly sufficient to account for the phenomena of fermentation, as the bodies which are undergoing fermentation do not 'enter into the same state' as the particles of the ferment; but they apply admirably to many of the illustrations cited by Liebig in proof of his theory. Amongst these illustrations is an experiment by Saussure, who observed that moist woody fibre, if placed in contact with oxygen, gradually converts the oxygen into carbonic acid. On adding a certain quantity of hydrogen to a measured bulk of oxygen, which was undergoing this change, he observed a diminution in the volume of the two gases immediately after effecting the mixture; a portion of oxygen had thus been caused to enter into combination with the

hydrogen, and a true gradual combustion of the hydrogen had been effected, analogous to that produced by platinum, owing to its contact with vegetable matter, which was itself undergoing slow oxidation.

Again, it has been observed in the case of certain alloys, that the compound is entirely soluble in an acid which may be unable to attack one of the components of the alloy when in a separate form. Platinum, for instance, is not soluble in nitric acid, but if it be alloyed with 10 or 12 parts of silver, the acid dissolves it readily. In like manner, copper is insoluble in dilute sulphuric acid, but an alloy of zinc, nickel, and copper is readily dissolved by this liquid.

(862) *Effects of Motion on Chemical Affinity.*—In many cases motion favours the manifestation of cohesion in a remarkable manner: for example, water may be cooled below its freezing point, and may retain its liquid form if kept perfectly motionless, but on the slightest agitation it assumes the form of ice. Again, a solution of nitrate of silver be simply mixed with hydrochloric acid, it will long remain milky; but if the nitrate be in excess, and the mixture be briskly shaken for about a minute, the whole of the chloride of silver will collect in dense flocculi, which rapidly subside, and leave the liquid clear. In a somewhat similar manner motion favours the development of chemical action:—thus a mixture of tartaric acid and nitrate of potash may be made, and no sign of precipitation will appear for many minutes, if the mixture after simple agitation be left at rest: but if it be briskly stirred with a glass rod, an abundant deposition of crystals will speedily be produced. A similar effect is often observed with other crystalline precipitates: the double chloride of platinum and potassium, or of platinum and ammonium, frequently does not appear in dilute solutions until the mixture has been briskly stirred. If the glass rod which is used in stirring the mixture be drawn against the side of the vessel containing the liquid, the track of the rod will be rendered evident by the formation of crystals, which are symmetrically deposited on each side of this line. This effect is particularly manifested when a solution of phosphate of soda is added to dilute neutral solutions of magnesia containing ammoniacal salts; the double phosphate of ammonia and magnesia takes many hours for its deposition, unless the liquid be briskly stirred.

Sometimes when the chemical affinities which hold a compound together are feeble, or where the components have a strong tendency to assume the gaseous form, a blow will be sufficient to disturb the equilibrium, and an explosion will follow. In this way chloride of nitrogen, which is united by feeble affinities, and

contains bodies which naturally exist in the gaseous state, is sometimes decomposed by the mere fall of a drop of the liquid to the bottom of a jar of the solution in which it is being formed. The ordinary percussion cap is another instance of the same kind, where the nitrogen in the fulminic acid suddenly resumes its gaseous state on the application of a blow. In the latter case, and in that of the common lucifer match, it might be supposed that the heat developed by the sudden compression attending the blow or the friction, is the cause of these detonations; but this explanation certainly cannot apply to the iodide of nitrogen, which, if dry, explodes when touched even with a feather. Fulminating silver is also decomposed with explosion by causes equally slight.

(863) *Concurring Affinities*.—Another class of these so-called catalytic phenomena is exemplified in the effect of the admixture of oxide of copper, or oxide of manganese, in aiding the decomposition of chlorate of potash. Chlorate of potash fuses at about  $550^{\circ}$  F., and when heated to about  $700^{\circ}$  it is decomposed with effervescence and rapid evolution of oxygen: when mixed with about a fourth of its weight of black oxide of copper, or of oxide of manganese, the salt begins to be decomposed at a temperature of between  $450^{\circ}$  and  $500^{\circ}$  (much below its fusing point); the gas which is given off in this case, however, is always accompanied by a small quantity of chlorine. Other oxides produce a similar effect, but the temperature required varies with each oxide: thus, sesquioxide of iron requires a temperature of about  $500^{\circ}$ ; oxide of lead a somewhat higher temperature; whilst oxide of zinc, and magnesia do not aid the decomposition of the salt at all.

This remarkable decomposition appears to admit of an explanation, suggested by Mercer, in elucidation of other somewhat analogous actions. He supposes, although the catalytic body experiences no perceptible alteration after the decomposition is complete, that it acts by exerting a feeble chemical affinity upon one of the constituents of the compound. In the case of oxide of manganese and chlorate of potash, the oxide of manganese is a substance which has an affinity for an additional quantity of oxygen, as is evinced by the possibility of forming manganic and permanganic acids from it by further oxidation. This tendency, although it does not rise high enough in the experiment before us to produce the acids, may yet exert sufficient attraction upon the oxygen to facilitate its escape. Indeed it is not impossible that traces of manganic acid may be actually formed, and then decomposed; in which case the formation of the small quantity of potash, and the

liberation of the chlorine, which always accompanies the oxygen, would be accounted for. A somewhat similar explanation may be applied in the case of the black oxide of copper; an unstable sesquioxide of this metal appears to exist; black oxide of copper therefore has a feeble affinity for oxygen, and though that affinity is not adequate to retain the oxygen when separated from the chlorate of potash, it may yet aid in effecting its liberation: sesquioxide of iron is also susceptible in the ferric acid, of a higher but unstable stage of oxidation, and the same holds good of oxide of lead; hence these compounds facilitate the decomposition of the chlorate. There is no proof of the existence of a higher oxide either of zinc, or of magnesia, and accordingly we find that scarcely any effect is produced on heating these oxides with the chlorate. I find also that powdered glass and pure silica are equally inert, probably from the same cause.

Mercer observed that starch, which is ordinarily converted by nitric acid into oxalic acid, is entirely transformed into carbonic acid if a salt of manganese be present;  $2\text{CO}_2$  being formed, instead of  $\text{C}_2\text{O}_3$ . Oxalic acid, also, may be in this manner rapidly converted into carbonic acid (Playfair *On Catalysis, Proceed. Chem. Soc.*, III. 351). If an ounce of oxalic acid be dissolved in 10 ounces of water, at  $180^\circ\text{F}$ ., and 1 ounce of colourless nitric acid, sp. gr. 1.30, be added, no decomposition of the oxalic acid occurs; but it immediately commences on adding a small quantity of a solution of nitrate, or any other salt of manganese. The protoxide of manganese, from its tendency to pass into the state of peroxide, tends to deprive the free nitric acid of oxygen, and aids the oxalic acid to decompose this acid; and the oxalic acid having a stronger affinity for oxygen than the protoxide of manganese, immediately appropriates the oxygen; the united affinities of both being able to accomplish a decomposition which could not have been effected by either separately. This reaction appears to be analogous in nature, though inferior in amount, to that which enables chlorine to decompose silica or alumina when these oxides are mixed with charcoal, (388, 566,) though neither chlorine nor charcoal is able separately to produce this effect.

A similar result is obtained when a quantity of hydrated oxide of copper, or of peroxide of manganese, is thrown into a mixture of bleaching powder and water; on warming the mixture, oxygen is evolved abundantly, and chloride of calcium is formed, the oxide of copper or of manganese, by its affinity for oxygen, aids the elastic force developed by heat in detaching the oxygen from

the chloride of lime, and the oxygen, by its elasticity, escapes in the gaseous form without combining with the metallic oxide.

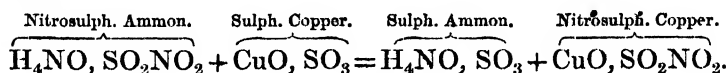
Gaseous ammonia may be passed through heated porcelain tubes at a very high temperature, and it will experience only a partial decomposition; but if the tube be filled with finely divided metallic copper or iron, the decomposition takes place with facility at a lower temperature. It is not improbable that in this case the metals act by their affinity for nitrogen, which is feeble, and that a nitride of copper may be formed (448). If iron wire be employed instead of finely divided iron, it is found to have become superficially altered and brittle. Platinum favours the decomposition of ammonia but slightly, and glass scarcely in any appreciable degree.

Alcohol, when exposed to the air, evaporates without undergoing any chemical change, but if a quantity of caustic potash be dissolved in the alcohol, the alkali appears to enhance its affinity for oxygen; in consequence of which acetic and formic acids are produced, and combine with the potash.

The decomposition of binoxide of hydrogen (396) by contact with many bodies, which appear to undergo no chemical alteration during the action, may possibly be referred to the same cause. When, for example, finely divided metallic gold, silver, or platinum, or peroxide of manganese, is placed in the liquid binoxide, the latter is decomposed, the oxygen being attracted by the metal, which, however, has not sufficient power to retain it in combination. A singular circumstance, however, has been observed, when oxide of gold or oxide of silver is substituted for the metals themselves; decomposition of the binoxide is produced by the metallic oxide, but the oxide of gold or of silver at the same time parts with its oxygen, and is reduced to the metallic state. A similar reaction happens if an acid solution of bichromate of potash be mixed with the binoxide of hydrogen, the chromic acid losing half its oxygen simultaneously with the binoxide of hydrogen.\*

\* Prof. Brodie (*Phil. Trans.* 1850, p. 759) has published the results of a series of experiments, showing that in such decompositions there is a numerical relation between the quantity of the binoxide which is decomposed and of the metallic oxide which is reduced. These experiments, however, were chiefly made upon binoxide of barium, as being much more manageable than binoxide of hydrogen. It was found that when the binoxide was mixed with water, and placed in contact with oxide, or chloride of silver, that both the compound of barium and that of silver was decomposed; baryta, or chloride of barium, being formed, whilst metallic silver and oxygen gas were liberated. A uniform quantity of peroxide of barium was employed in each experiment, whilst the quantity of oxide, or of chloride of silver, was progressively increased: it was found that the silver compound was never wholly reduced, but that the proportion of it which

Other substances besides binoxide of hydrogen, exhibit a similar susceptibility to decomposition by contact with certain bodies. Persulphide of hydrogen, for example, is immediately decomposed by contact with oxides of manganese and silver, and like the binoxide of hydrogen, it is rendered more stable by the addition of acids, while its decomposition is facilitated by contact with alkalis. The nitrosulphates (354) discovered by Pelouze, afford another instance of decomposition effected by a body which undergoes no *apparent* change; but this decomposition is particularly instructive, as it is almost certain that the body which excites the decomposition does suffer a *real* chemical change. Thus the addition of a solution of sulphate of copper to solution of nitrosulphate of ammonia, causes an immediate effervescence, owing to the escape of protoxide of nitrogen. This decomposition appears to be produced thus:—on the addition of sulphate of copper, the nitrosulphate partially exchanges bases with it; now so long as the nitrosulphuric acid is in combination with an alkali, the acid has a certain stability, since the alkalies appear by their basic energy to preserve the elements of the acid in equilibrio, but as soon as a salt with a weaker base is added, such as the sulphate of copper, a portion of nitrosulphate of copper is formed, but the oxide of copper being no longer able to maintain this balance, the elements of the acid arrange themselves in a new order: for instance—



But the nitrosulphate of copper immediately breaks up into protoxide of nitrogen and sulphate of copper;  $\text{CuO, SO}_2\text{NO}_2$  becoming  $\text{CuO, SO}_3 + \text{NO}$ . Consequently sulphate of copper is found in the liquid at the close of the reaction *apparently* unaltered.

underwent decomposition bore an increasing ratio to the amount of peroxide of barium which was decomposed, as the quantity of oxide, or of chloride of silver was increased. In no case, however, was the amount of oxide or of chloride of silver reduced quite equivalent to the proportion of oxygen eliminated from the peroxide of barium. Prof. Brodie connects these experiments with an ingenious speculation, by which he endeavours to account for the simultaneous liberation of oxygen from the peroxide of hydrogen or of barium and from the oxide of silver, and which he applies to chemical decompositions generally: he supposes that the *particles of the same element* may, in certain circumstances, have an affinity for each other;—that for example, one equivalent of the oxygen of the peroxide of barium may be positive in its relation to the oxygen of the oxide of silver, which he supposes may be negative. In such a case the two particles of oxygen would mutually attract each other, and decomposition of both the oxides would be the result, \*

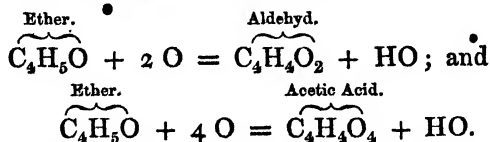
## § 2. INFLUENCE OF HEAT UPON CHEMICAL AFFINITY.

(864) The forces which have as yet been considered do not manifest any specific effect in altering the amount of chemical affinity between any two bodies; but it is quite otherwise in the case of heat, which exerts a direct influence upon the degree of affinity. Elevation of temperature generally acts at once in augmenting the tendency to combination between the bodies which are submitted to its influence:—for example, sulphur or charcoal may be preserved at ordinary temperatures, in air or in oxygen, without change, for an indefinite period; but if sulphur be heated to  $500^{\circ}$ , and charcoal to a point a little below a red heat, oxidation commences, and proceeds with increasing vigour, and the phenomena of combustion occur. But although a rise of temperature exalts the action of chemical affinity, this tendency to combination is, at the same time, more or less counteracted, and is sometimes, completely overcome, by the tendency to mutual repulsion which it imparts to the molecules of all substances, both simple and compound. It not unfrequently happens that a moderate elevation of temperature produces combination, whilst a higher temperature destroys the compound so formed. A good instance of this kind occurs in the action of oxygen upon mercury: at ordinary temperatures this metal shows no disposition to combine with oxygen, for it evaporates in air and condenses again in the metallic form; but at a temperature approaching  $700^{\circ}$ , or a little above the boiling point of the metal, it combines gradually with oxygen and becomes converted into the red oxide; whilst at a heat short of redness it is decomposed into gaseous oxygen and vapour of mercury. Again—baryta at a red heat absorbs a second equivalent of oxygen, forming peroxide of barium, but the second equivalent of oxygen is expelled by a full white heat, and the compound is reconverted into baryta. A mixture of oxygen and hydrogen may be preserved unchanged at ordinary temperatures, but the introduction of a glass rod heated to bare redness so completely alters their mutual affinity, that sudden combination attended with explosion is the result. This appears to be as pure a case of alteration of affinities as can be met with, since both the components are thoroughly mixed, and as both are in the gaseous state, heat cannot in this case act by diminishing cohesion, and so bringing their particles into more intimate contact. Mr. Grove, however, has shown that in the case of this same compound of oxygen and hydrogen a sudden inversion of affinity

takes place, for at an intense white heat they are separable from each other: by the voltaic ignition of a platinum wire under water, or by the intense heat of a ball of melted platinum raised to whiteness by an alcohol flame animated by a current of oxygen, and then plunged under water, the two gases may be separated from each other and collected in the gaseous state (*Phil. Trans.*, 1847).

Sometimes the decomposition effected by elevation of temperature is only partial; a new and more stable compound being formed, which, at a still higher temperature, is in its turn decomposed: thus olefiant gas at a full red heat loses half its carbon, and is converted into light carburetted hydrogen; and this gas, if subjected to a white heat, deposits the remainder of its carbon whilst pure hydrogen is liberated. Chlorate of potash at a moderate heat is decomposed into perchlorate, and probably into chlorite of potash; the latter salt, however, is immediately resolved into oxygen and chloride of potassium; but at a higher temperature the perchlorate in its turn parts with its oxygen, and the more stable chloride of potassium is the final result. Numerous other instances of this kind will be presented to the reader when the products of organic chemistry are examined.

A further illustration of this point is afforded by the different products which are furnished by the combustion of the same body at different temperatures. When a jet of cyanogen is burned with a free supply of air, the only products of the combustion are carbonic acid and nitrogen; but if a coil of red-hot platinum wire be suspended in a mixture of equal volumes of cyanogen and oxygen, the nitrogen undergoes oxidation as well as the carbon, deutoxide of nitrogen being formed, as is evidenced by the appearance of ruddy fumes, owing to the combination of the deutoxide with free oxygen. In a similar manner, ether, when burned freely in air, produces carbonic acid and water,  $C_4H_5O + 12 O = 4 CO_2 + 5 HO$ ; but if a glowing coil of platinum wire be suspended in a mixture of the vapour of ether and atmospheric air, several new products are formed, among which are aldehyd and acetic acid:—



(865) *Suspension of Chemical Action by Depression of Temperature.*—As chemical affinity is increased, on the one hand, by elevation of temperature, so, on the other hand, it is diminished by reduction of temperature. Schrötter has shown (*Chemie*, vol. I.,



p. 129) that, by a sufficient degree of cold, chemical combination may be prevented even between bodies which at the ordinary temperature of the air unite with each other with great energy. Chlorine, for example, combines with phosphorus, or with finely-divided metallic antimony, or arsenic, with such violence, that these bodies take fire spontaneously in an atmosphere of the gas; but if the chlorine be cooled down to  $-106^{\circ}$  F., by means of a bath of solid carbonic acid and ether (182), it remains liquid at the ordinary pressure of the air, and it is then quite indifferent to the phosphorus, arsenic, or antimony, if these substances be cooled to the same temperature before they are added to the liquid chlorine. When the tube in which the mixture is contained is withdrawn from the cold bath, the evaporation of the chlorine occurs with sufficient rapidity to preserve the temperature below the point of combination; but if the free escape of the chlorine be prevented, the temperature rises, and combination occurs with explosive violence. The mutual action of chlorochromic acid and alcohol, of chlorine and ammonia, of iodine or of bromine and phosphorus, and various other actions of a similar nature, may be prevented in the same way.

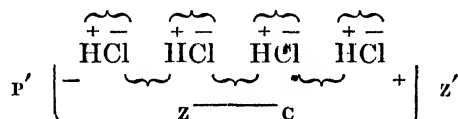
From these experiments, and from those detailed in the foregoing paragraph, it appears to be not improbable that when two bodies have an affinity for each other, there is a certain range of temperature within which they will enter into combination, but if the temperature be raised or depressed beyond a certain limit, their mutual affinity is suspended; and at high temperatures the compound already formed may be destroyed. The temperature most favourable for combination varies with each pair of bodies, and it seems to be probable that there is for each, a certain temperature at which the maximum of affinity exists, above or below which it decreases.

### § III. INFLUENCE OF ELECTRICITY ON CHEMICAL AFFINITY.

#### ELECTROTYPING, VOLTAIC PLATING, &c.

(866) The suspension of chemical action which occurs under the influence of electrical induction is one of the most interesting circumstances which modern discoveries have brought to light. As an instance of this kind we may cite the manner in which zinc, when placed in contact with copper beneath the surface of sea water, acts in preventing the corrosion of the copper, and

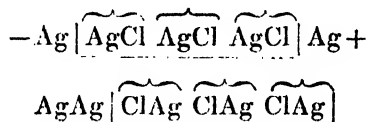
transfers to itself the chemical energy which would otherwise be manifested upon the copper (229). A similar suspension of chemical action is produced in the ordinary case of the decomposition of water between two platinum electrodes, by the voltaic current: here the electricity appears to act by weakening or rather by partly neutralizing ordinary affinity in one direction, whilst it strengthens or adds to it in the opposite, and hence the particles, which were previously in combination with each other, lose their affinity one for the other, and acquire it for those particles which are next adjacent to them in the liquid; thus, if the brackets above the subjoined formulæ indicate the state of combination of the elements of hydrochloric acid before the passage of the current, the brackets below would indicate the effect produced after its transmission, thus:—



Here z c is supposed to represent the battery, and p' and z' the platinode and zincode of the arrangement: the positive electricity of the zincode seems to detach the chlorine adjacent to it from the hydrogen with which it was previously in combination, whilst the negative electricity of the platinode produces a similar effect upon the contiguous particles of hydrogen, and the intermediate portions are polarized in the manner represented in the foregoing diagram.

The following modification of this experiment also shows in a striking manner the remarkable influence of electric polarity upon chemical affinity:—If two separate glasses filled with dilute sulphuric acid, be placed side by side, and into one glass the platinode of the battery is plunged, whilst the zincode dips into the other cell, no decomposition will ensue; but if a connexion be established between the two glasses by means of a slip of platinum foil, one end of which is made to dip into each, the current will be immediately transmitted: hydrogen will be evolved upon the platinode in one glass, and oxygen upon the zincode in the other glass; whilst owing to the polar condition to which the connecting slip of platinum is thrown, hydrogen will be given off from one end of the slip, and oxygen will be evolved upon the other extremity of it, although the metal itself experiences no sensible change.

(367) *Electrolysis of Salts*.—It has already been stated (24<sup>1</sup>), that when a binary compound, such as a fused chloride, or an iodide, is submitted to electrolysis, the ions or components of the compound are separated at the respective electrodes in equivalent proportions; the metal appearing at the platinode, whilst the chlorine, or corresponding element, is deposited at the zincode. If the zincode of the battery be formed of a substance capable of combining with the chlorine or corresponding element, an equivalent amount of the chloride, or other compound, of this metal will be formed there: when the metal of the zincode is the same as that contained in the compound which is undergoing decomposition, the original compound is reproduced. Thus, if a quantity of fused chloride of silver ( $\text{AgCl}$ ) be decomposed by a current, which is conducted into it by means of silver wires, the quantity of the chloride will undergo no alteration; for in this experiment as fast as the silver is deposited upon the negative wire a corresponding amount of silver will be dissolved from the positive wire, since the latter wire combines with the equivalent quantity of chlorine, which is liberated at this point. Let  $\text{Ag}+$  represent the positive silver wire, or zincode, by which the current is conveyed into the melted chloride, and  $\text{Ag}-$  the negative wire: if the brackets in the upper row of symbols which follow indicate the combination before the passage of the current, the lower ones will show the arrangement after the occurrence of the decomposition:—

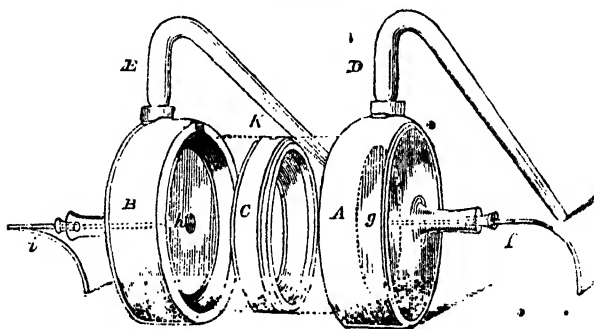


An examination of the products furnished by the electrolytic decomposition of solutions of the oxysalts in water, exhibits results which appear to be at variance with the statement that the components of an electrolyte are separated in equivalent proportions, but further investigation shows that they are strictly in accordance with it; these experiments also lead to very interesting conclusions which have an important bearing upon the theory of salts in general.

When a solution such as sulphate of soda is submitted to electrolysis, a quantity of acid accumulates around the positive plate, and of alkali around the negative plate, whilst at the same time both oxygen and hydrogen are set free. The proportions of each may be determined by means of a diaphragm apparatus, in

which the products of decomposition can be kept separate from each other, and the gases which are evolved can be separately collected. Such an apparatus was contrived by Professor Daniell, and is represented in fig. 321. A and B are the two halves of a stout glass cylinder, which are fitted by grinding upon a hollow ring of glass, c; the two rims of this ring are ground down to a grooved shoulder, so as to allow a thin piece of bladder to be tied over each end of the ring, which thus constitutes a kind of drum; at k is a small hole through which the cavity thus formed ~~can~~ be filled with liquid; d and e are two bent glass tubes for carrying off the gases evolved during electrolysis; g and h are two large platinum electrodes, which pass through corks in the necks of the cylinder, and can be connected with the battery by means of the

FIG. 321.



wires, *f, i*. The apparatus thus forms three compartments, which may be filled with liquid for experiment, and the whole may be supported in a frame of wood. By the employment of this apparatus, it is found that whilst a quantity of acid accumulates at the zincode, an equivalent amount of alkali is set free at the platinode. But this is not all, a quantity of gas is also emitted from each electrode, that from the zincode being oxygen, and that from the platinode, hydrogen. Upon placing a voltameter in the course of the circuit, it is found that a quantity of gas is emitted from the saline liquid, exactly equal to that obtained from the voltameter; and upon neutralizing the acid and alkali, they likewise are in equivalent proportions to the gas which is emitted (Daniell, *Phil. Trans.*, 1839 and 1840). Suppose that the gas collected in the voltameter amount to 71 cubic inches, (or the quantity yielded by 9 grains of water at 60° F., Bar.=30 inches.) The united quantity of oxygen and hydrogen from the solution of sulphate of soda would

be the same, and in addition, one equivalent in grains, or  $\frac{1}{71}$  grains of sulphate of soda would be decomposed; 31 grains of soda would be liberated at the platinode, and 40 grains of sulphuric acid at the zincode. Upon substituting a voltameter of fused chloride of lead in the circuit for one containing diluted sulphuric acid, and still continuing to transmit the current through the solution of sulphate of soda, it was found that for every equivalent of chloride of lead which was decomposed, 1 equivalent of the mixed gases were evolved from the saline solution, and at the same time 1 equivalent of the sulphate was decomposed. What is observed in the case of sulphate of soda holds good also with salts of the alkalies and earths generally.

(868) *Bearing of Electrolysis on the Binary Theory of Salts.*—It is a fundamental law of voltaic action, that the amount of force circulating in any circuit at the same time, is equal in every vertical section of the circuit, and consequently its decomposing energy in each section must also be equal; yet in the case of the sulphate of soda, there appears to be in the saline solution twice the amount of decomposition that occurs in the adjacent voltameter, though both are transmitting the entire current from the battery. A satisfactory and complete explanation of this anomaly is however effected by the *binary theory* of salts (454) in the following manner:—

If the binary theory of salts be true, the component ions of sulphate of soda are not soda and sulphuric acid ( $\text{NaO}, \text{SO}_3$ ), but sodium and sulphion (a compound of 4 equivalents of oxygen and 1 of sulphur), ( $\text{Na}, \text{SO}_4$ ), the compound being *sulphonide of sodium*; and such it proves to be under the influence of electrolysis, sodium being liberated at the platinode, whilst sulphion appears at the zincode. Sodium, however, cannot exist in the presence of water; the metal immediately takes oxygen, and becomes converted into soda;  $\text{Na} + \text{HO} = \text{NaO} + \text{H}$ : the alkali is dissolved in the liquid, whilst the hydrogen escapes as gas. Sulphion is equally unable to exist in the separate form; it combines with hydrogen,  $\text{HO} + \text{SO}_4 = \text{O} + \text{H}, \text{SO}_4$ , while oxygen escapes, and sulphuric acid is formed: and as both sodium and sulphion are liberated in equivalent proportions, the quantity of water decomposed is also equivalent to the quantity of salt electrolysed.

On the foregoing view, therefore, the evolution of oxygen and hydrogen during the decomposition of saline solutions is a secondary action. If a solution of a salt of a metal, which like copper or lead does not decompose water at ordinary temperatures, be substituted for one of sulphate of soda as the electrolyte, no hydrogen should be

evolved, but the metal itself should appear upon the platinode, whilst if the other constituent of the salt be one which like chlorine is unable to take hydrogen from water at common temperatures, no oxygen should be emitted. Accordingly, upon making the experiment with a solution of chloride of copper or of chloride of lead, the salt is resolved into metallic copper or metallic lead, and chlorine gas, but no oxygen or hydrogen is liberated. These observations will explain the reason that although water, when pure, is scarcely decomposed by the current from 100 cells or upwards, but it appears instantly to become a good electrolyte on the addition of a few drops of acid, or of solution of a salt of an earth or an alkali; for upon the addition of the salt it is this body which is decomposed, and the water is then resolved into oxygen and hydrogen by a secondary action in the manner already explained. Sulphuric acid in solution is in like manner resolved into hydrogen and sulphion,  $\text{H}_2\text{SO}_4$ . In neither case is the water directly electrolysed. This observation also explains a circumstance which much perplexed the earlier experimenters upon the chemical action of the voltaic pile. In all experiments in which water was decomposed, both acid and alkali were invariably found to be liberated at the electrodes, although distilled water was employed; and hence it was believed for some time that the voltaic current had some mysterious power of generating acid and alkaline matter. The true source of these compounds, however, was traced by Davy (*Phil. Trans.*, 1807), in which he showed that they proceeded either from impurities contained in the water employed, or in the vessels made use of, or in the atmosphere itself. Having proved that ordinary distilled water always contains traces of saline matter, he distilled it at a temperature below the boiling point, in order to avoid all risk of carrying over salts by splashing: he found that when he used marble cups to contain the water for decomposition, the acid was the hydrochloric, and the alkali was soda derived from chloride of sodium contained in the marble itself; when agate cups were used to contain the water he obtained silica; and when he used gold vessels, he procured nitric acid and ammonia, which he traced to atmospheric air; by operating in vacuo, the quantity of acid and alkali was reduced to a minimum, but the decomposition then was almost arrested, although he operated with a battery of 50 pairs of 4-inch plates. Hence it is manifest that water itself is not an electrolyte, but it is enabled to convey the current, if it contain only faint traces of saline matter.

The following table will illustrate the manner in which the oxysalts may be classified in relation to their mode of electric

decomposition; the *anion* indicating the electronegative, the *cation* the electropositive component:—

A, Simple	.	.	.	{	Simple Anion . . . . .	Ag, Cl.
					Simple Cathion . . . . .	
B, Complex	I. Monobasic.	1.	Simple Anion . . . . .	}	NH <sub>4</sub> , Cl.	
			Compound Cathion . . . . .			
		2.	Compound Anion . . . . .	}	K, SO <sub>4</sub> .	
			Simple Cathion . . . . .			
		3.	Compound Anion . . . . .	}	NH <sub>4</sub> , NO <sub>3</sub> .	
			Compound Cathion . . . . .			
	II. Polybasic.	1.	Compound Anion . . . . .	}	3 Na, PO <sub>3</sub> .	
			Simple Cathions . . . . .			
		2.	Compound Anion . . . . .	}	(Na, H, NH <sub>4</sub> ), PO <sub>3</sub> .	
			Simple and Compound Cathions . . . . .			

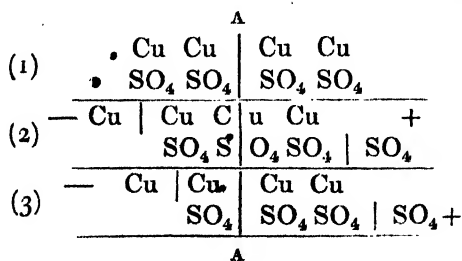
When *monobasic salts* are the subjects of electrolysis, the proportion of acid and of base is in single equivalents: thus, nitrate of potash yields 1 equivalent of potash and 1 of nitric acid for each equivalent of fused chloride of lead which is decomposed in the voltameter.

When a *polybasic salt* is submitted to electrolysis, for each equivalent of fused chloride of lead which is electrolysed in the voltameter, an equivalent of base appears at the platinode: for example, when 1 equivalent of the tribasic phosphate of soda is decomposed, 3 equivalents of chloride of lead are reduced in the voltameter; and in the diaphragm cell 3Na, PO<sub>3</sub> yield 3NaO + 3H at the platinode, whilst PO<sub>3</sub> + 3O are liberated at the zincode. When the pyrophosphate of soda (2NaPO<sub>3</sub>) is electrolysed, 2 equivalents of chloride of lead are decomposed in the voltameter, whilst 2NaO + 2H make their appearance at the platinode of the diaphragm cell, and PO<sub>3</sub> + 2O are set free at the zincode. When the metaphosphate of soda (Na<sub>3</sub>PO<sub>3</sub>) is decomposed, 1 equivalent of chloride of lead is electrolysed in the voltameter, whilst NaO + H appears at the platinode of the diaphragm cell, and PO<sub>3</sub> + O is liberated at the zincode. In each case the phosphoric acid thus transferred preserves its tribasic, dibasic, or monobasic character, according to the nature of the salt which was electrolysed.

The results of the electrolysis of the monobasic and polybasic oxysalts, it will thus be seen, admit of a simple explanation upon the binary theory. The results of the decomposition of the subsalts are not however so easily reconciled with this view. According to E. Becquerel, when basic salts (or subsalts) are decomposed, for each equivalent of chloride of lead in the voltameter, 1 equivalent

of acid is liberated at the zincode, whilst all the equivalents of base which were previously in combination with the acid are liberated at the platinode. My own experiments upon this point confirm this view, although from a numerous series of trials on the subnitrites, subnitrate, and subacetates of lead, I always obtained a smaller quantity of oxide of lead and of metallic lead than was required by theory, if this law held good; probably this deficiency was due to the secondary action of the solution upon the liberated oxide. When, for example, the triacetate of lead ( $3 \text{ PbO}$ ,  $\text{C}_4\text{H}_3\text{O}_3$ ) was decomposed, employing as the electrodes plates of lead instead of plates of platinum, for each equivalent of acetic acid and oxygen which appeared at the zincode, somewhat less than 1 equivalent of metallic lead and 2 equivalents of oxide of lead appeared at the platinode: thus, the salt appeared to have undergone decomposition into  $\text{Pb}$ ,  $2 \text{ PbO}$  and  $\text{C}_4\text{H}_3\text{O}_3\cdot\text{O}$ . It is difficult to reconcile the idea of an ion consisting of  $\text{Pb}$ ,  $2 \text{ PbO}^*$  with the binary theory. The most probable explanation appears to be this: viz., that the oxide of lead is attached to the neutral acetate in a manner analogous to water of crystallization, and that the neutral acetate is the true electrolyte, whilst the oxide is left upon the electrode in the insoluble form, as soon as the acid which kept it in solution is removed. A similar explanation may be applied to the case of other soluble subsalts.

(869) *Unequal transfer of Ions during Electrolysis*.—A curious circumstance in relation to the proportion in which the ions of the electrolyte travel towards the respective electrodes, was remarked in the course of these investigations on the decomposition of saline solutions. It was perhaps natural to expect that if a solution underwent electrolytic decomposition, for each equivalent of the compound decomposed, its component ions should be transferred to each electrode in the exact proportion of half an equivalent of each, although a whole equivalent was liberated in the manner shown at No. 2, in the scheme which follows:—



A

\* E. Becquerel considered that he had obtained a new suboxide of lead by the electrolysis of its subsalts, but this appears to be an error. It is a mere



In this scheme it is supposed that sulphate of copper is the electrolyte, each particle of copper represented by the symbol  $\text{Cu}$ , being in combination with the particle of sulphion represented by  $\text{SO}_4$  immediately beneath it. Let  $\text{A A}$  indicate the position of a diaphragm of bladder separating two equal quantities of the solution which in No. 1 are supposed to be in their normal state. Let No. 2 represent the same solution after it has undergone electrolysis; an equivalent of copper having been set free at the platinode, and one of sulphion at the zincode. It was not unnatural to expect that this result would have been attained by the transfer of half an equivalent of copper into the division containing the platinode, whilst half an equivalent of sulphion passed towards the zincode, in the manner represented. Experiment, however, shows that such a supposition is erroneous, and that the decomposition more commonly happens in the mode represented in No. 3, in which case a whole equivalent of the anion is transferred to the zincode, leaving a whole equivalent of cation uncombined, at the platinode. Sometimes when the oxide of a metal is soluble in water, the transfer of a small quantity of the cation takes place towards the platinode, but the quantity of the cation and the anion set free are always in equivalent proportions to each other (*Phil. Trans.* 1844, p. 16).

(870) *Electrovection, or Electrical Endosmose*.—It was observed many years ago by Mr. Porrett, when water was placed in a diaphragm apparatus one side of which was connected with the positive, and the other side with the negative electrode of the battery, that a considerable portion of the liquid was transferred from the positive towards the negative side of the arrangement. It has since been found that the same result occurs in a minor degree when saline solutions are electrolysed, and generally the greater the resistance which the liquid offers to electrolysis the greater is the amount which is thus mechanically carried over. From numerous experiments I have found that in all these cases the water carries with it a proportion of the salt which it holds in solution. It appears from the researches of Wiedemann (*Poggendorff, Annal.*, lxxxvii., 321), that the amount of liquid transferred, *cæteris paribus*, is proportioned to the strength or intensity of the current; that it is independent of the nature and thickness of the diaphragm by which the two portions of liquid are sepa-

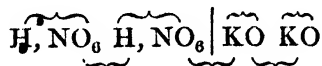
mixture of metallic lead with oxide of lead, as the solution of neutral acetate of lead quickly dissolves the oxide and leaves the metallic lead; and the proportions of oxide to the metallic lead vary according to the nature of the salt operated upon.

rated; and that when different solutions are employed, the amount transferred in each case by currents of equal intensity, is directly proportional to the specific resistance of the liquid.

In some cases I have found a transfer from the negative to the positive side of the apparatus. This was particularly the case with solutions of sulphate of magnesia and of sulphate of zinc. The cause of this transfer, and the circumstances which occasionally produce the reversal of its direction, have not been satisfactorily explained, and the subject needs further investigation.

Acids, whether they be soluble in water or not, always travel towards the zincode in proportions larger than the metals which are united with them pass towards the platinode.

(871) *Secondary results of Electrolysis.*—The explanation already given of the mode in which the oxyalts are electrolysed was happily applied by Professor Daniell to the elucidation of the origin of the voltaic power, in a combination contrived by M. Becquerel (230) which presents many interesting peculiarities. If a porous tube filled with nitric acid be plunged into a vessel containing a solution of potash, and the wires of a galvanometer, armed with platinum plates, be plunged one into the nitric acid, and the other into the alkaline solution, a current will circulate; oxygen will be emitted from the plate immersed in the potash, and nitrous acid, owing to the absorption of hydrogen by the nitric acid, will be formed around the other plate, whilst nitrate of potash is slowly produced by transudation of the two liquids through the pores of the diaphragm. By connecting several of these cells together in succession, upon the principle of the ordinary battery, the power may be considerably augmented. The decomposition which appears to occur is represented by the following symbols, in which  $H, NO_6$  indicates the nitric acid, and  $KO$  the potash: the position of the brackets above the symbols indicates the arrangement before the current is established, whilst, after its passage, the arrangement is supposed to be that indicated by the brackets beneath:—



It is particularly to be observed that no development of oxygen or of hydrogen occurs upon the platinum plates until the two plates are united by a conducting wire, and it ceases as soon as the conducting communication between the plates is interrupted, although the combination of the potash with the nitric acid continues; but the polar arrangement of the particles is interfered with.

The secondary action of nitric acid on the hydrogen which is set free is necessary to the development of the current. If sulphuric acid be substituted for nitric, the hydrogen is not absorbed, and no current is obtained, as it is neutralized by the counter current which the accumulation of the hydrogen upon the platinum plate tends to produce (231).

The secondary actions of the voltaic current are often of great importance; they require to be carefully distinguished from its primary effects. Secondary results are, in some instances, produced by the action of the liberated components of the electrolyte upon the materials employed as electrodes: thus, if a slip of copper be substituted for platinum, as the zincode of the battery, and be immersed in dilute sulphuric acid, sulphate of copper will be formed by the combination of the copper with the disengaged sulphurion. At other times, the secondary results are manifested by the reaction of the ion upon the liquid in which the electrolyte is dissolved, as when the potassium or sodium, set free at the platinode in an aqueous solution of its salts, liberates hydrogen by removing oxygen from the water. In the cases just cited, the affinities of the disengaged ions are very intense, and the secondary action is exactly proportioned to the primary, so that it may be employed as a measure of the current: but when the tendency to combination is more feeble, the proportion of these secondary actions to the primary one is greatly influenced by the extent of surface exposed by the electrode to the liquid, and the energy of the current, and consequent quantity of the ion disengaged at once. Generally, the slower the action, and the larger the surface of the electrode, the more uniform and complete is the secondary action. These results are well exemplified by Bunsen's researches on the isolation of the more oxidizable metals by the voltaic current. If a thin platinum wire be used as the platinode in a solution of chloride of chromium, to convey the current from 4 or 5 cells of the nitric acid battery, metallic chromium may be obtained without difficulty; but if a plate of platinum be employed, oxide of chromium, mixed with a certain amount of hydrogen, is liberated; in the latter case the metal has time to decompose the water before fresh particles of chromium are deposited upon its surface.

In consequence of these secondary actions, the same element may sometimes appear at one electrode, sometimes at the other, as is seen in the case of nitrogen: if, for instance, a solution of sulphate of ammonia be submitted to electrolysis, it yields hydrogen at the platinode, and a mixture of nitrogen with oxygen

is set free at the zincode. The nitrogen in this case is a secondary result of the combination of a portion of the oxygen with the hydrogen of the ammonia. If nitrate of ammonia be substituted for the sulphate, nitrogen appears among the gaseous products at both electrodes, the nitric acid being deprived of its oxygen by the hydrogen evolved at the platinode, and the ammonia of its hydrogen by the oxygen set free at the zincode.

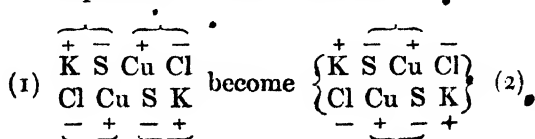
If a solution of acetate of lead be employed as the electrolyte, the acetic acid undergoes partial decomposition from the action of the oxygen upon it at the moment of its liberation at the zincode, but at the same time a portion of the oxygen also enters into combination with some of the oxide of lead contained in the liquid, and, as Mr. Warington proved, a deposit of peroxide of lead is produced. Nobili, who first observed this phenomenon, found that if a polished steel plate be employed in such a solution as the zincode to the battery (4 or 6 cells of Grove's may be employed), the deposit assumes the form of a thin film, which exhibits the iridescent tints of Newton's scale, the tints varying according to the thickness of the film produced. Other experimentalists have modified the patterns which may be obtained by these *metallochromes*, which have even been applied by Becquerel to the imitation of the tints of flowers; and by varying the strength of the battery and of the solutions employed, he has succeeded in producing some effects of great delicacy and beauty. Salts of manganese or of bismuth may be substituted for those of lead, with similar results.

Many of these secondary actions are very interesting: Kolbe has devoted particular attention to the effects of oxygen when liberated during electrolysis (*Proceedings, Chem. Soc.*, III., 285, and *Quart. Journ. Chem. Soc.*, II., 157). Hydrochloric acid, especially when previously mixed with sulphuric acid, is in this manner partially converted around the zincode into chloric and perchloric acids; and in an acid solution of chloride of potassium, chlorate and perchlorate of potash are formed. Cyanide of potassium in solution, when subjected to the voltaic current, is in like manner converted into the cyanate. A concentrated solution of chloride of ammonium evolves hydrogen at the platinode, but the chlorine, instead of being liberated at the zincode, acts upon the chloride of ammonium, and forms oily drops of chloride of nitrogen, which explode when touched by the opposite electrode. Mr. Smee has shown that by means of the voltaic current the yellow prussiate may be converted into the red prussiate of potash. M. Kolbe has, further, ascertained the effect of the liberated oxygen upon

various organic compounds, and by submitting valerianate of potash to electrolysis he decomposed the valerianic acid ( $\text{HO}, \text{C}_{10}\text{H}_{17}\text{O}_3$ ) which it contains, and succeeded in obtaining from it a new substance, *valyl*,  $\text{C}_8\text{H}_9$  (or more properly *butyl*); a new ether,  $\text{C}_8\text{H}_9\text{O}$ , *butylic ether*, and a carbo-hydrogen ( $\text{C}_8\text{H}_8$ ), apparently identical with oil gas (405): and by a similar process from acetic acid ( $\text{HO}, \text{C}_2\text{H}_3\text{O}_2$ ) he obtained methyl,  $\text{C}_2\text{H}_3$ , the analogue of butyl. Particular interest is attached to these researches, owing to the circumstance that in each case the compounds obtained by the electrolysis belong to a series related to an alcohol different from that which was submitted to decomposition. The valerianic acid thus yields an ether of the butylic series; and acetic acid, which is a derivative of wine alcohol, furnishes the carbo-hydrogen which belongs to the wood spirit series.

(872) *Nascent state of Bodies*.—It is obvious, from the powerful effect which oxygen produces at the moment of its liberation from compounds during electrolytic decomposition, that such oxygen must be in a condition very different from that in which it exists when once it has assumed the gaseous form. Oxygen is not insoluble in water, and it is therefore possible to bring it in small quantities at a time into chemical contact with salts or other bodies which water may hold in solution. Oxygen gas may, however, be transmitted for an unlimited time through a solution of chloride of potassium without effecting the conversion of any portion of the chloride into chlorate, or into perchlorate of potash; and yet, as has been mentioned in the foregoing paragraph, this change is easily effected by oxygen as it escapes during the electrolysis of an acidulated solution of the chloride of potassium. But it is not necessary that oxygen should be liberated by the agency of the voltaic battery in order that it should acquire this increase of activity. If hydrated protoxide of nickel, or protoxide of cobalt, be suspended in a solution of potash, it will undergo no change when subjected to a current of oxygen gas; but if a current of chlorine be substituted for the oxygen, the whole of the metallic oxide will be converted into a brown sesquioxide: this change arises from the action of the chlorine upon the potash, during which, chloride of potassium is formed, whilst oxygen is set free, and, at the moment of its liberation, attaches itself to the oxide of nickel or of cobalt;  $\text{KO} + \text{Cl} + 2 \text{NiO} = \text{KCl} + \text{Ni}_2\text{O}_3$ . Other substances besides oxygen exhibit this peculiarity, and chemists have long recognised the fact, that bodies, when in this *nascent state*, that is to say, when in the act of liberation from other substances, display more energetic affinities than they

sh~~ow~~ when once obtained in the isolated form:—For example, cyanogen and chlorine do not enter directly into combination; but if cyanogen, at the instant that it is set free from another compound, be presented to chlorine, the two bodies combine; thus if moist cyanide of mercury be decomposed by means of chlorine, chloride of cyanogen may be obtained: the chlorine removes the mercury step by step, and the cyanogen, at the moment of its liberation, enters into combination with another portion of chlorine. In a similar manner, sulphur, when set free from an alkaline persulphide in the midst of a solution of hydrochloric acid, combines with hydrogen, and forms persulphide of hydrogen,  $\text{KS}_5 + \text{HCl} = \text{KCl} + \text{HS}_5$ , the chlorine taking the potassium, whilst the sulphur and the hydrogen, both in the nascent state, unite to form a new compound, although their affinity is so slight that this compound spontaneously separates into sulphuretted hydrogen and free sulphur. The process of double decomposition is particularly applicable in cases where the mutual affinity of the bodies which it is desired to obtain in combination is comparatively feeble. It is not impossible that this superior chemical activity of bodies in the nascent state may arise from the fact that their particles are individually electrified at the moment of their separation from a previous state of combination; and that in this condition they may exert upon the particles of dissimilar contiguous matter, a force of induction which may be the agent that determines their chemical combination: if by a process of double decomposition the particles of both compounds were oppositely electrified, combination might be expected to be proportionably facilitated:—For instance, if a solution of sulphide of potassium and one of chloride of copper be mixed, they will mutually decompose each other, the sulphur being negative, will tend to combine with the positive copper, and the positive potassium will unite with the negative chlorine. If the brackets in No. 1 represent the mode in which the molecules are arranged on the instant of mixture previous to decomposition, those in No. 2 will illustrate the arrangement of the molecules after mutual decomposition has been effected:—



(873) *Theory of the Electrical Origin of Chemical Affinity.*—It has already been remarked (214, 225) that whenever two dissimilar substances, electrically insulated, are brought into contact, and

are separated from each other; disturbance of their electrical equilibrium is produced; one of the bodies becoming negatively electrified, whilst the other indicates a corresponding charge of positive electricity. It is a well ascertained fact that certain substances, by friction, acquire one kind of electricity more readily than the other; thus, for example, sulphur, when rubbed upon flannel or fur, becomes negatively electric, whilst glass, on the other hand, most readily, assumes the positive state. What has been proved to occur when masses of matter are brought into contact was supposed by Davy (*Phil. Trans.*, 1807), to happen also when the molecules of two dissimilar substances are brought within the sphere of mutual activity; he assumed that, chemical and electrical attractions depend upon the same cause, acting in one case on particles, in the other on masses of matter' (*Phil. Trans.*, 1826, p. 369); and all the phenomena of chemical affinity have been referred to the exertion of mutual electrical attraction between the atoms of each substance in the compound. When, for example, chlorine and potassium are united, it is supposed that each atom of chlorine, by contact with an atom of potassium, becomes negatively electrified, whilst the potassium becomes positively excited; a certain portion of the positive electricity from the chlorine uniting with a corresponding amount of negative electricity which is liberated from the potassium, thus producing the light and heat which attends the combination of these two bodies (Berzelius). Supposing each atom of both kinds of matter to be associated with equal quantities of both electricities, and that the two different electricities be represented by the signs + and -, we may represent the potassium and chlorine by symbols; ( $-K +$ ) indicating an atom of potassium, and ( $-Cl +$ ) an atom of chlorine. As soon as the two bodies are brought into contact, it is supposed that the chlorine loses a certain amount of positive electricity, whilst the potassium loses an equal quantity of negative electricity, the change being symbolized thus, ( $+KCl -$ ) and ( $+ -$ ). When the chloride of potassium is decomposed electrolytically, a quantity of positive electricity is transferred from the positive wire of the battery to the chlorine, and compensates for that which it has lost; and when this amount of electricity has been restored, the chlorine no longer has any tendency to remain in combination with the potassium, and hence it is set free upon the positive plate, whilst a simultaneous transfer of negative electricity to the potassium occurs from the negative plate, and the alkaline metal is therefore liberated upon the negative side of the arrangement. The electricity which is set free

by the battery is supplied by the action of the sulphion upon the zinc, in the cells of which the battery consists.

The remarkable law discovered by Faraday, that the same current of electricity, when transmitted successively through various electrolytes, decomposes each in the proportion of their respective chemical equivalents (247, 4) adds greatly to the probability of the supposition that electrical and chemical phenomena are due to different manifestations of the same agent. So strong was Daniell's conviction upon this point, that he applied the term *current affinity* to the voltaic current; since by means of the proper application of conductors, or channels for the force, the chemical affinity of a portion of zinc and sulphuric acid at one point could be transferred to a distant spot; and could there be made to effect an equivalent amount of chemical decomposition upon a different compound. The chemical equivalent of any substance upon the electro-chemical theory, is that quantity of each body which is associated with an amount of electricity equal to that associated with a given weight of some substance, such as hydrogen, which is selected as the standard of comparison; the proportion of electricity which is associated with a given weight of any substance being inversely as its atomic weight. Assuming the specific electricity of hydrogen to be represented by the arbitrary number 1000, the following is given by Daniell (*Introd. to Chem. Phil.*, 2nd Ed., p. 687) as an approximative table of the *specific electricity* (or quantity of electricity associated with *equal weights*) of a few of the more important elements and compounds:—

Cathions.	Equiva- lent.	Specific Electricity.	Anions.	Equiva- lent.	Specific Electricity.
Hydrogen . . .	1.0	1000	Oxygen . . .	8.0	125
Potassium . . .	39.2	25	Chlorine . . .	35.5	27
Sodium . . .	23.3	43	Iodine . . .	126.0	8
Zinc . . .	32.5	31	Bromine . . .	78.3	12
Copper . . .	31.6	31	Fluorine . . .	18.7	55
Ammonia . . .	17.0	58	Cyanogen . . .	26.0	38
Potash . . .	47.2	21	Sulphuric Acid . . .	40.0	25
Soda . . .	31.3	32	Nitric Acid . . .	54.0	18
Lime . . .	28.5	35	Chloric Acid . . .	75.5	13

Ingenuous, however, as is the electrical theory of chemical affinity, it must be admitted that it is far from being free from objection and difficulty when it is attempted to apply it to all cases of chemical action. It has been already stated that a very large number of bodies exist which are not susceptible of electrolysis. Indeed, the chief classes of electrolytes are: 1, binary



compounds of the non-metallic elements with the metals, such as the oxides, chlorides, iodides, bromides, and fluorides; 2, compounds of bodies like cyanogen with the metals, such as the cyanides and the sulphocyanides; and 3, compounds of the metallic oxides with the oxyacids, such as the nitrates, sulphates, borates, carbonates, acetates, tartrates, &c. Now, so long as a compound consists of two elements only, if it be decomposed at all, there is no difficulty in anticipating the result of the voltaic action;—the electro-negative element will appear at the zincode, and the electro-positive element at the platinode; yet there are binary compounds which are not electrolysable, such, for instance, as pure water, and chloride of sulphur. If their particles be united by electric opposition, why should they not yield to the current? In the case of more complex bodies, such, for example, as nitrate of silver, or borate of lead, it is not possible, *à priori*, to say how the compound would yield under the electric influence. It is quite clear in the case of a salt, that the power which holds together the two ions of the salt in the form of two *iso-electric* groups (or groups of equal electric energy), must be of a different order from that which holds the elements of its component ions in combination. The tie which binds together nitrate of silver as  $\text{Ag}, \text{NO}_3$ , must be of a different order to that which unites the elements of *nitron* ( $\text{NO}_3$ ) together. Sulphate of soda, again, as an electrolyte is separated into  $\text{Na}$  and  $\text{SO}_4$ . But neither nitron nor sulphion can exist in the separate form; how can they become associated under electric influence? Again,  $\text{SO}_3$ , anhydrous sulphuric acid, is not an electrolyte when fused: the same thing may be said of fused boracic acid; and examples of this kind might be multiplied almost without limit. Why, if chemical affinity be due to the exertion of electric action, should certain bodies be readily decomposable by the voltaic current, and why should others of less complex composition resist it entirely? At present, no hint appears to have been given which throws any satisfactory light upon these questions.

#### *Practical Applications of Electrolytic Action.*

\*(874) *Electrotype, Voltatype, or Galvano-Plastics.*—Professor Daniell, shortly after his invention of the constant battery, observed that copper deposited upon a plate of platinum furnished a coherent sheet, in which the lines and irregularities on the surface of the platinum were faithfully reproduced upon the deposited copper, but he made no practical application of the observation. In the year 1839, M. Jacobi, of St. Petersburg, announced that he had discovered a method of making exact copies of a metallic

surface in copper by means of the voltaic battery, and shortly afterwards Messrs. Spencer and Jordan, who had each independently arrived at a similar result, published the methods which they had employed for the attainment of this object. The processes thus disclosed were so simple and easy of execution that they were immediately repeated with success, and in the following year Mr. Elkington in England, and M. Ruolz in France, began to apply the voltaic battery on an extensive scale to the arts of plating and gilding. Since this period the voltaic battery has been most extensively employed as a means of depositing not only copper, gold, and silver from their solutions, but zinc, tin, lead, platinum, and nickel: many other metals have also, for particular purposes, been reduced from their salts by its means.

For the deposition of metallic copper, a solution of the sulphate of this metal is employed, but the mode of using it varies with the object in view. Suppose that it be desired to obtain a copy of an engraved copper plate; a wire or slip of copper having been soldered to the plate for the purpose of facilitating its connexion with the battery, the back of the plate is covered with a resinous varnish, by which means this surface is electrically insulated from the solution, and it is thus protected from any deposit of reduced metal. The plate thus prepared is connected with the negative electrode of a voltaic battery, consisting of 3 or 4 of Smee's or Daniell's cells, and immersed vertically in a bath consisting of a saturated solution of sulphate of copper. A sheet of copper, equal in size to the one to be copied, is suspended parallel to the latter in the liquid, and connected with the positive electrode of the battery; an immediate decomposition of the solution ensues; metallic copper is deposited upon the entire surface of the negative plate, in the form of a coherent, continuous sheet, and a corresponding amount of copper is dissolved from the positive plate, so that the liquid remains constantly charged with an equal quantity of sulphate of copper. At the commencement of the operation, care must be taken to ascertain that the deposit occurs uniformly over the whole surface of the negative plate, as if any portion of it be soiled by grease or resinous matter, the copper will not be thrown down upon those parts; when once the deposition has commenced uniformly, it goes on without difficulty. If the plates be suspended vertically the solution should be frequently agitated, for unless this precaution be taken, the liquid around the negative plate becomes impoverished, whilst that around the positive plate becomes unduly saturated with the copper salt. (869); currents are then produced in the liquid, owing to its unequal density, and

they occasion the formation of vertical grooves and striae upon the back of the sheet of deposited metal. This inconvenience is sometimes obviated by supporting the two plates in the bath in a horizontal position, the negative plate being undermost; the positive plate must in this case be enveloped in flannel, in order to prevent the small particles of metal, which are constantly being detached from it, from falling upon the lower plate, and interfering with the regularity of the deposition.

The deposit varies in hardness and coherence according to the number of cells employed in the battery; the relative size of the plates of the battery and those of the depositing cell, and the temperature and degree of concentration of the solution. The more slowly the action takes place if the solution be concentrated, the harder and more crystalline is the deposit. By modifying the power of the battery, and the strength of the solution, in the manner which experience soon indicates, copper may be obtained of any desired degree of toughness.

When the deposit has acquired the necessary thickness, it is detached at its edges from the original plate, and can then be stripped off without difficulty. The thin film of oxide, or of other adhering impurity, derived from the exposure even of a freshly deposited copper plate to the air for a few hours, is sufficient to prevent too intimate an adhesion between the plate and the deposit. In the electrotype thus obtained, the lines which are cut away upon the surface of the original plate are represented in relief in the copy, and if a fac-simile of the engraving be desired, a new deposit must be formed upon the copy thus procured; in this second transfer an exact duplicate of the original engraving will be presented. Many large and valuable copper plates, amongst which are some of those engraved for the Art Union, have been thus multiplied with success. So faithfully does the deposit reproduce all irregularities upon the surface of the matrix on which it is deposited, that copies of daguerreotype plates have been obtained by its means, in which the original design is accurately transferred to the deposit of copper, without destroying the original impression.

(875) *Preparation of Moulds for Electrotyping.*—In copying medals or other works of art, it is frequently necessary to employ casts of the objects instead of the original objects themselves, which might be liable to injury by immersion in the metallic solution. These casts may be made in fusible metal, or in stearine, in plaster, or gutta percha. Mr. Gore (*Pharm. Journal*, July, 1855) recommends a mixture of 2 parts of gutta percha and 1 of marine glue; the materials are to be cut up, and the glue melted at a gentle

next and incorporated with the gutta percha. The paste is to be applied whilst soft, with a pressure gradually increasing, to the surface of the medal, or other object which it is desired to copy. In certain cases an impression of the object to be copied is obtained in sheet lead by the application of strong pressure. In all cases the back of the mould must be coated with a resinous varnish, or with some non-conducting matter. When moulds of plaster of Paris are employed they must be rendered impervious to moisture by immersion in melted wax or tallow; after which the surface to be copied is endued with the power of conducting electricity, by an ingenious method suggested by Mr. Robert Murray: it consists simply in applying finely powdered black-lead, of good quality, to the surface by means of a brush, taking care that every portion of the surface to be copied is completely coated by it. The cast is then connected with the negative wire of the battery by means of a strip of sheet lead, or a copper wire, which is in electric contact with some portion of the black-lead surface. Impressions of seals in sealing wax, stamps in relief upon pasteboard or paper, and the engraved blocks used for woodcuts, thus rendered conductors upon the surface, may be electrotyped with facility. Even glass may be rendered a conductor by the use of Drayton's method of depositing silver upon its surface (793). Leaves, flowers, fruits, and insects have also been coated with copper, or with silver, by the electrotype process. A method of producing a conducting surface upon these articles, due I believe to Captain Ibbetson, consists in immersing them in a weak solution of phosphorus, either in bisulphide of carbon or in ether, allowing the solvent to evaporate from the surface, and then plunging the objects into a solution of nitrate of silver; the phosphorus left upon the surface reduces a very thin film of silver upon the superficial portions of the objects, sufficient to enable them to receive the deposit from the battery, if they be properly connected with the negative wire, and submitted in a metallic bath to the action of the electric current. Steel plates cannot be copied by immersing them in a bath of sulphate of copper, as the steel and the sulphate act chemically on each other, and thus the engraving would be destroyed. This difficulty has been overcome by electrotyping them first in silver, which can be deposited upon the steel without injury, and upon this silver matrix a copper facsimile of the original plate can afterwards be obtained.

The voltaic current has also been employed for the purpose of biting in the plates of the engraver, instead of the nitric acid commonly used for this purpose. Both sides of the plate

are first coated with engraver's varnish, after which ~~the~~ <sup>the artist</sup>, with a fine point, etches in the usual manner the lines which he intends to produce upon the plate, cutting through the coating of varnish so as to expose the metallic surface beneath; when the design is thus completed the plate is connected with the *positive* wire of the battery; and on completing the circuit, the oxygen and acid liberated upon the surface of the plate will attack those portions of it which have been exposed by the tool of the engraver.

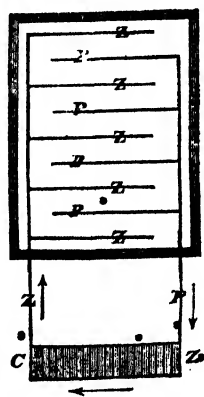
For the electrotyping of small objects, such as coins or medals, it is not necessary to use a separate voltaic battery, since the depositing cell itself may be converted into a voltaic couple of sufficient power to decompose the sulphate of copper, in the following manner:—Let a glass cylinder, such as the chimney of an argand gas burner, be closed below by a plug of plaster of Paris, and be supported in a vessel containing a solution of sulphate of copper, in which the mould of the medal to be copied is supported by a metallic wire; let the inner tube be filled with sulphuric acid, diluted with 10 or 12 times its bulk of water, and let an amalgamated zinc rod be placed in its axis. If this zinc rod be connected with the wire proceeding from the mould of the medal to be electrotyped, copper will be deposited upon the surface of the mould. The apparatus in fact constitutes a cell of Daniell's battery, with a trifling modification in its form. The solution of copper should be maintained uniformly saturated with sulphate of copper, by suspending crystals of the salt in the upper part of the liquid.

(876) *Electro-zincing*.—Zinc may be deposited from its sulphate on the surface of iron, by processes similar to those used for sulphate of copper. The operation requires but a feeble current, and admits of being performed upon a very large scale: the iron links of the Charing Cross suspension-bridge, which are passed into the abutments on the side of the river, were successfully submitted to this operation: each of these links is 24 feet in length, and of proportionate width. It is not possible however to obtain coherent plates of all the metals with the same facility as in the case of copper and zinc. Many of the metals are thrown down from their solutions in a crystalline form, whether the deposition be effected rapidly or slowly. Silver is separated thus from its nitrate, and lead exhibits a similar deportment when the acetate or the nitrate of this metal is electrolysed. Gold and platinum do not give coherent plates when solutions of the chlorides of these metals are submitted to voltaic decomposition. In some cases, however, where a simple salt fails to give a satisfactory result, the effect may be obtained

by the employment of certain double salts of the same metal with potash or with soda: thus the double cyanide of gold and potassium is largely employed for gilding, and the corresponding salt of silver is extensively used in electro-silvering. In gilding and silvering, and zincing, one great desideratum is to obtain a firm adherence between the newly deposited metal and the object to be gilt or plated; the surface of the metallic object is therefore first rendered *chemically clean*, a result which is carefully avoided in the process of electrotyping. In the latter case it is usual to expose the object, if freshly polished, to the atmosphere for 24 hours before placing it in the depositing cell, in order to prevent permanent adhesion.

(877) *Electro-Plating*.—The metals upon which an adherent coating of silver is most readily deposited are brass, copper, bronze, and German silver; but it may also be effected on steel. The articles to be plated are cleansed from adhering greasy matters either by boiling them in a weak alkaline solution, and then washing; or they are heated to low redness in a muffle: in either case they are next dipped into dilute nitric acid for the purpose of removing any adhering film of oxide. They are then brushed with a hard brush and some sand; and having been rinsed from adhering impurities, and separately attached to a clean copper wire, they are again dipped into nitric acid, washed, and immersed whilst still wet in the silvering bath. If *v v*, fig. 322, represent a plan of this bath, and *c z* the voltaic battery, the copper wires attached to the articles to be plated are twisted round the rods *p p p*, which are connected with the negative wire of the battery, whilst the positive wire is connected with a series of silver plates, *z z z*, which are also immersed in the silvering liquid. This solution is commonly prepared by dissolving cyanide of silver in a solution either of cyanide or of ferrocyanide of potassium. Solutions containing hyposulphite or sulphite of silver are occasionally employed. In order to prepare the silvering bath a solution of nitrate of silver may be precipitated by the addition of cyanide of potassium so long as it produces a precipitate; this precipitate, after having been washed by decantation, is dissolved in a solution of cyanide of potassium. An excess of cyanide of potassium is requisite, at least 3 parts of cyanide of potassium being employed for 1 part of

FIG. 322.



cyanide of silver.\* A solution which contains  $\frac{1}{10}$  of its weight of silver is found to be of a convenient strength for ordinary operations. When cyanide of potassium is used in the bath as a solvent, the solution gradually becomes alkaline from the formation of carbonate of potash, which accumulates in the liquid and interferes with the regularity of the decomposition. Now it has recently been discovered that if cyanide of calcium be employed, this inconvenience is obviated, since carbonate of lime is formed, and owing to its insolubility, it sinks to the bottom of the bath as fast as it is produced. The articles when plated have a dead white or chalky surface, but they may be burnished by pressure if desired, and they then assume the brilliant lustre of polished silver. It is remarkable that the addition of a very small proportion of bisulphide of carbon to the bath causes the deposited silver to assume the lustre of the polished metal.† The amount of silver which is deposited can be regulated very accurately by weighing the articles before immersion; and weighing them again afterwards. A deposit of from  $1\frac{1}{4}$  ounce to  $1\frac{1}{2}$  ounce of silver to a square foot of the plated surface answers well in practice; the sheet of silver under these circumstances being about the thickness of ordinary writing paper. The solution must be frequently stirred in order to preserve the liquid of uniform density and composition throughout.

The batteries used at Birmingham for gilding and silvering are in general simply plates of amalgamated zinc opposed to plates of copper in dilute sulphuric acid: the plates are so arranged that they can be readily raised or lowered in order to expose a smaller or larger surface to the action of the acid. The superficial area and number of the plates used, are made to vary according to the size and nature of the objects to be operated upon. The workman judges from experience as to the number of pairs to be employed; it seldom happens that more than two or three pairs of plates

\* If ferrocyanide of potassium be used as a solvent of the cyanide of silver, 10 parts of this salt are required for the solution of 1 part of cyanide of silver.

† In order to effect this object, 6 ounces of bisulphide of carbon are directed to be agitated with 1 gallon of the plating liquid, and set aside for 24 hours. Two ounces of the liquid thus obtained, are to be added over night to 20 gallons of the ordinary plating liquid; the bath is ready for use next morning. This addition of the solution of the bisulphide requires to be renewed daily, to make up for the loss of the bisulphide of carbon by evaporation. Much care is required in the use of such a solution, as it is liable to changes which are produced by very slight modifications in the mode of working.

are needed. In Paris, Bunsen's carbon and zinc batteries are also employed with success in these operations.

(878) *Electro-Gilding and Platinizing*.—It is possible to gild most of the ordinary metals by voltaic action. Articles which consist of brass, bronze, copper, or German silver are first annealed, then *pickled*, as the operation of immersing them into the mixture of dilute nitric and sulphuric acids is termed, after which they are scrubbed and 'dipped' in strong nitric acid, and then rinsed in water, as is practised in preparing them for plating. Silver articles are cleansed in a similar manner, but they do not require to be 'dipped.' Iron and steel may be gilt by cleansing them from grease, first with potash, and then by dipping in nitric acid, and scouring the surface with burnt clay finely sifted, in order to remove the black stains produced by the liberation of carbon. A more powerful current is required for gilding upon iron than upon the metals previously mentioned.

The gilding bath most usually employed, consists of cyanide of gold dissolved in cyanide of potassium. It may be prepared by dissolving gold in aqua regia, and adding cyanide of potassium to the diluted liquid as long as it produces a precipitate; a brisk effervescence accompanies the action, and a yellow deposit of proto-cyanide of gold ( $\text{AuCy}$ ) is formed: the clear liquid is decanted, and the precipitate is redissolved in a solution containing between 7 and 8 parts of the cyanide to 1 part of gold: the solution is then diluted until 100 parts of the liquid contain 1. part of gold.

M. Ruolz has shown that various other gilding baths may be used instead of the double cyanide of gold and potassium: for example, he finds that the cyanide of gold may be employed when brought into solution by the ferrocyanide, or by the ferridecyanide of potassium; he has also used with success the double sulphite of gold and soda, the solution of the double chloride or iodide of gold and sodium with an excess of soda, and even the sulphide of gold dissolved in a neutral solution of protosulphide of potassium.

As yet the voltaic deposition of platinum has not been practised to any considerable extent; it is stated, however (*Comptes Rendus*, vol. xiii., p. 1013), that a solution of the double chloride of platinum and potassium in caustic potash may be applied to this purpose with tolerable success.

#### 4. INFLUENCE OF LIGHT ON AFFINITY—PHOTOGRAPHY.

(879) *Influence of Light upon Crystallization*.—It is a familiar



observation, that volatile bodies which crystallize as they are condensed after spontaneous sublimation,—such as camphor, naphthalin, and sesquichloride of carbon,—if placed in glass vessels, collect upon the side of the glass which is exposed to the light, whilst no crystals are deposited upon the other side of the vessels. This effect, however, is not confined to crystallizable substances. If a few drops of water be placed at the bottom of a bottle, the sides of which are kept dry, and the mouth of the bottle be closed, on placing it in the sunshine for a few minutes a deposit of globules of moisture will speedily take place upon the illuminated side of the bottle. A similar effect is often seen in the vacuum of a barometer, globules of mercury being condensed upon the side of the tube which is exposed to light. Dr. Draper (*Chemistry of Plants*, Appendix, p. 124), has made a number of observations on these phenomena, from which it appears that the transmission of light through an aperture in a metallic screen, or the reflection of the light from a surface of glass, and other apparently trifling modifications of the light, will prevent the deposition of vapour in such cases. The whole subject is well worthy of further investigation.

(880) *Chemical Actions of Light*.—The rays of the sun are not only the great source both of heat and light to the globe which we inhabit, but they are constantly exerting upon the various substances upon its surface, a chemical influence of the utmost importance to the existence of animal and vegetable life, and to the permanence of the present order of creation. The occurrence of this remarkable chemical activity in the solar rays may be shown in various ways:—When perfectly dry chlorine is mixed in the dark with hydrogen, no chemical change takes place; if the two gases have been exposed separately to the beams of the sun, and have subsequently been mixed in the dark, they may be preserved in this condition also without change, so long as they are screened from the light; but if the mixture be exposed to diffused daylight, it will be observed that the two gases begin gradually to combine, and if they be free from admixture with hydrochloric acid, sudden combination and explosion occurs when they are exposed to the direct rays of the sun. The rapidity with which this combination occurs is proportioned to the intensity of the light, and an instrument for measuring the amount of the action which is produced by diffused daylight, was described by Dr. Draper, under the somewhat fanciful name of the *tithonometer* (*Phil. Mag.*, Dec. 1843).

A. similar combination, under the influence of sunshine, is effected between chlorine and the carbonic oxide gas. Two measures of chlorine and two of carbonic oxide are thus condensed into 2 measures; the result is the formation of the irritating pungent gas, known as phosgene gas (327), in allusion to the mode of its production. It is remarkable that the direct union of these gases cannot be effected in any other manner.

Organic chemistry abounds with instances in which combinations and decompositions are effected by chlorine, under the influence of the solar ray: a few of these have been mentioned when speaking of the transformations of Dutch liquid, (400). But the chemical actions produced by the sun's rays, which are taking place unperceived around us, are of infinitely greater importance than those limited transformations which can be effected in the laboratory; for it is upon these unobserved, yet daily renewed alterations, that the growth and renovation of the entire vegetable kingdom is dependent. The great chemical effect of light appears to be that of a powerful reducing or deoxidizing agent. Under the influence of solar light, the green parts of plants perform their allotted function in the purification of the atmosphere, by absorbing and removing carbonic acid, in virtue of which they fix the carbon in their tissues, and thus supply themselves with food; by a similar decomposition of water they obtain the hydrogen needed for their growth, while they return into the aerial ocean a portion of the oxygen with which the carbon and the hydrogen were previously in combination, and thus assist in maintaining that uniformity in the composition of the atmosphere which is indispensable to the healthful existence of animal life.

If solar light be excluded from plants, none of these decompositions are effected; the carbonic acid escapes unchanged into the air, and no fixation of carbon ensues; the plant becomes pale and succulent, whilst its functions languish. Gardeners take advantage of this knowledge in order to procure vegetables of more delicate flavour; by earthing up the plant, as is practised with celery, or by covering it with a tile as in the case of endive, or by enclosing it in a bell jar, as is usual with sea-kale, the light is more or less excluded, and the bleaching which is desired in vegetables for the table is produced. The operation of bleaching linen, by exposure to moisture and light for several weeks during summer, is another process, which illustrates the influence of solar light in the production of chemical changes.

(881) *Reducing Influence of Light on Metallic Salts.*—Much

attention has, within the last few years, been given to the study of the chemical actions produced by light, in consequence of the beautiful inventions of the Talbotype and the Daguerreotype. These remarkable processes, as well as others of a somewhat similar character, appear to depend upon the power which the more refrangible rays of the solar spectrum possess of causing the decomposition of the oxides, chlorides, iodides, or bromides of silver, and of one or two other of the metals. This decomposition by means of light, however, only takes place under the concurrent influence of hydrogen, or some metallic body, which acts either by setting free the silver or other metal, or by producing a lower oxide, chloride, or other compound of the metal. The alteration in the composition of the compound, after its exposure to light, is not always manifested at once by change of colour, but it may be rendered visible by the reactions produced by the application of suitable chemical reagents to the compound after it has been so exposed to the solar ray.

The following instances of the effects of light have long been observed by chemists:—If a piece of white silk be dipped into a solution of chloride of gold, and exposed whilst in a moist state to the sun's light, the silk becomes green, then purple, and in less than an hour a film of metallic gold is produced upon its surface. Nitrate of silver in solution in pure water undergoes no change when exposed to the light, but if any organic matter be added to the liquid, a black deposit is gradually formed; and if the salt be placed upon the surface of the skin, upon paper or upon linen, the well-known blackening effect for which it is valued as a marking ink for linen is produced. Moist chloride of silver retains its dazzling whiteness if preserved in total darkness, but it assumes a violet tint, which gradually deepens in intensity if exposed, particularly when in a moist state, even to the diffused light of day, a portion of chlorine being liberated in the process.

(882) *Photographic Printing*.—The earliest experiments upon the production of pictures by the action of light, appear to have been made by Wedgwood and Davy in the year 1802. Wedgwood moistened white paper or white leather, with a solution of nitrate of silver, and by its means copied paintings on glass, and took profiles; but neither he nor Davy was able to devise any means for preserving these pictures when exposed to diffused light.

Little was published upon this subject until the commencement of the year 1839, when Mr. Fox Talbot made known (*Phil. Mag.* vol. xi.) his process of *photogenic drawing*, which consisted in

soaking ordinary writing-paper in a weak solution of common salt, and when dry, washing it over upon one side with a solution of nitrate of silver, consisting of 1 part of a saturated solution of the nitrate with 6 or 8 parts of water. This operation was performed by candle-light, and the paper was dried at the fire; in this manner a film of chloride of silver, mixed with an excess of nitrate of silver, was formed upon the surface of the paper. Suppose that it were desired to obtain a copy of an engraving, or of the leaf of a tree; one of the sheets so prepared was laid under the leaf or engraving which was to be copied; the two were pressed firmly together between two plates of glass, and exposed to the direct rays of the sun, or even to diffused daylight, for a period of half an hour or an hour. The impression thus obtained was a *negative* one, that is to say, the shadows were represented by lights, and the lights by shadows; those portions of the surface which had been exposed to the strongest light becoming dark; in the half tints, where a feebler light had been transmitted, the blackening became less evident; and the parts corresponding to the deep shadows in the engraving remained white. Mr. Talbot fixed these pictures by immersing them in a strong solution of common salt. Considerable improvements have been introduced into this process since it was first published, but, in principle, this operation, which has been termed *photographic printing*, remains unchanged.

A very good paper for this kind of printing may be obtained as follows:—Prepare a solution of chloride of sodium or of chloride of ammonium containing 10 grains of the salt to each ounce of water. If French paper (which is sized with starch) is to be used, it will be improved by dissolving 1 grain of gelatine in each ounce of the solution of salt. Pour this liquid into a flat shallow dish, and having cut the paper into pieces of a convenient size, take a sheet of it by the two opposite corners, and bring it down upon the surface of the solution, so that the middle of the sheet shall be first moistened; then lower it gradually towards each corner so as to exclude air-bubbles. After the lapse of a minute it may be removed from the solution, and hung up to dry. In order to render the paper sensitive, prepare a solution of nitrate of silver containing 50 grains of nitrate to the ounce, and lay the sheet upon the surface of the solution in the same manner as before; in about three minutes' time the sheet may be removed: it must be raised by one corner with a pair of forceps tipped with sealingwax, allowed to drain, and hung up to dry. These operations must be performed in a darkened room.

Another sensitive paper, which is often used, may be prepared by forming a solution which contains 80 grains of nitrate of silver in each ounce of distilled water, and adding caustic ammonia until the precipitated oxide of silver is almost redissolved: the solution should be preserved in a dark place. The paper having been previously salted, is excited by this solution, by brushing it over with the solution, by means of a pledget of cotton wool. The paper is allowed to dry in the dark, and should be used immediately.

In order to protect the picture obtained upon either of these papers, from the further action of light, it is now usual to adopt the method introduced by Sir J. Herschel, which consists in soaking the picture in a solution of hyposulphite of soda; this salt combines with the undecomposed salt of silver, and renders it soluble: by washing the picture for two or three hours in water, the salts of silver are removed, and it is no longer susceptible of change when exposed to light.

(1883) *Talbotype, or Calotype Process*.—In 1841, Mr. Fox Talbot took out a patent for the very beautiful process to which his name has since been attached. In this remarkable operation Mr. Talbot prepares a surface of iodide of silver upon paper, which is not sensitive *per se* to the action of light. In order to render it sensitive, he washes it over with a mixture of nitrate of silver with gallic and acetic acids, and then exposes it in the camera to the object which he wishes to copy. After the lapse of a few minutes, (the time required varying with the intensity of the light,) he withdraws the paper from the camera. Unless the light has been very strong, no image is visible, or a mere outline only, but the compound has undergone a change of a very singular nature, for if the blank sheet be washed over with the mixture of nitrate of silver with gallic and acetic acids, on gently warming it a *negative* image appears with wonderful distinctness and fidelity, the portions which have been exposed to the strongest lights assuming the darkest tints. The development of the image appears in this process to be due to the reducing agency of the gallic acid, which acts more rapidly upon those portions of the paper which have been most freely exposed to the action of light. This dormant picture may be developed many hours or even days after it was produced, if the paper be preserved from the light. It seems as though the light, without actually producing a decomposition of the particles of the argentine compound upon which it falls, gives to them a particular condition of unstable equilibrium which predisposes them to decomposition when acted upon by a reducing

agent like gallic acid. The following are the details of the operation, with one or two slight modifications :—

1. *Preparation of the Iodized Paper.*—A sheet of smooth writing paper, such as that manufactured by Turner, of Chafford Mills, of uniform texture, and free from stains and spots, should be pinned upon a board by two corners, and brushed over uniformly with a solution of nitrate of silver, containing 33 grains of the salt in an ounce of distilled water ; the solution is best applied by means of a brush consisting of a flock of cotton wool partly drawn through a glass tube, which furnishes a convenient handle : whilst the paper is still moist, it is immersed in a bath of iodide of potassium, containing 20 grains of the iodide to an ounce of distilled water, taking care to avoid the occurrence of air-bubbles. In about two minutes, or as soon as the paper has acquired a uniform yellow colour throughout, it is transferred to a vessel of water, where it is allowed to soak for two or three hours, changing the water three or four times, so as to remove all the soluble salts : each sheet of paper is then to be hung up separately and allowed to dry. These operations may be conducted by candle-light or in diffused daylight. A stock of this paper may be prepared and kept for use.

2. *Exciting the Paper for the Camera.*—When required for the camera, prepare 1. a solution of *aceto-nitrate of silver* (consisting of 50 grains of nitrate of silver, 1 ounce of water, and  $1\frac{1}{2}$  drachm of glacial acetic acid), and 2. an aqueous solution of gallic acid saturated in the cold. Add 3 or 4 drops of each of these solutions to 1 drachm of distilled water, and apply the mixture freely with a pledget of cotton wool to the silvered surface of the iodized paper, and when well soaked remove the superfluous portion with a sheet of clean blotting-paper : the same sheet of blotting-paper must not be used twice for this purpose. Whilst still damp it is to be placed between the glasses of the camera slide. It will retain its whiteness for twelve hours or more.

3. *Exposure in the Camera.*—In order to take a landscape, a sheet of the prepared paper is exposed in the focus of the camera, and after a lapse of from five to fifteen or twenty minutes, according to the amount of light, the picture may be withdrawn.

4. *Development.*—The image is developed by brushing the paper over, by means of clean cotton wool, with a mixture of equal parts of the solution of aceto-nitrate of silver and of gallic acid. The two solutions must be mixed immediately before using, as they speedily undergo mutual decomposition. In a few minutes

the picture gradually begins to appear. Any part of the picture which seems wanting in distinctness may be washed over with fresh solution of nitrate of silver. The development should be effected by candlelight or in yellow light.

5. *Fixing the Impression.*—As soon as the picture ceases to acquire distinctness, it is to be well washed with water, and immersed in a saturated solution of hyposulphite of soda till the yellow tint of the iodide of silver has disappeared. It is then to be washed thoroughly for several hours in clean water, frequently renewing the water. Unless all traces of the hyposulphite of silver be removed, the picture will gradually lose its intensity. Mr. Talbot originally employed a solution of bromide of potassium for fixing these pictures, but the hyposulphite of soda is to be preferred. When dry, the photograph should be waxed by placing it between two sheets of blotting-paper saturated with white wax, and then passing a smoothing iron moderately heated over the whole. The negative pictures thus obtained may be employed to furnish *positive prints*, or prints with the lights and shadows as they occur in nature, by Mr. Talbot's original 'photogenic' process, or by printing upon a second sheet of the prepared Talbotype paper.\*

(884) *Photography on Collodion.*—An important modification of Talbot's process was introduced by Mr. Archer, who substituted for the iodized paper a transparent film of iodized collodion spread upon glass as the recipient of the negative picture. The process is rendered more certain, very much more rapid, the manipulation is simplified, whilst the positive pictures obtained by transference of the negative impression are much sharper in their outline. To prepare the bath of nitrate of silver, take of nitrate of silver 300 grains, dissolve the salt in 2 ounces of distilled water, and add 1½ grain of iodide of potassium dissolved in half a drachm of water, then add drop by drop a solution of carbonate of potash till a slight permanent turbidity is produced; afterwards add distilled water until the mixture measures 10 ounces; filter, and add 2½ minims of glacial acetic acid.†

\* For further details upon the subject of photographic printing, &c., the reader is referred to Hardwich's *Manual of Photographic Chemistry*.

† Ordinary nitrate of silver is apt to contain a trace of nitric acid, which it is desirable to neutralize, as an acid solution is much less sensitive to the action of light than a neutral one. It is still more important, however, not to have any alkaline reaction, and as carbonate of silver is slightly soluble in the nitrate, the addition of acetic acid is subsequently made to guard against this; the iodide of potassium is added in order to saturate the bath with iodide of silver; if this precaution were not taken, the film of iodized collodion would be liable to lose a portion of iodide of silver, since this salt also is somewhat soluble in nitrate of silver.

The following are the directions given by Mr. Hardwich for preparing the solution of iodized collodion, which is suitable for the formation of negative pictures:—Take of rectified ether, sp. gr. 0.750, 6 drachms; alcohol, sp. gr. 0.836, 2 drachms; soluble pyroxilin (from Swedish filtering paper),\* from 3 to 5 grains; iodide of potassium, from 4 to 5 grains. The iodide of potassium is to be dissolved in the alcohol before adding it to the mixture.

1. *Preparation of the Collodion Film.*—In order to make use of this solution, a plate of glass cut to the size required for the camera (after being washed with solution of potash to free it from grease, rinsed in water, dried, and wiped with a clean silk handkerchief), is to be held horizontally in the left hand, and a portion of the collodion is poured steadily on the middle of the glass, and by slightly inclining the plate in different directions, is made to flow completely over the upper surface; the excess of the solution is immediately to be poured back into the bottle.

2. *Exciting the Plate for the Camera.*—The nitrate bath having been introduced into a glass or gutta serena trough of sufficient width to allow the introduction of the glass plate upon which the collodion is spread, the prepared plate, within half a minute after the film has been poured over its surface, is introduced into the solution of nitrate of silver; in from 2 to 3 minutes' time it is thoroughly impregnated with iodide of silver, and when withdrawn from the bath it has assumed an opaque cream colour. These operations must be effected in a room illuminated by light admitted through a yellow blind, or by the light of a candle screened by yellow glass.

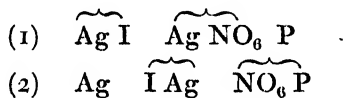
• 3. *Exposure in the Camera.*—The prepared plate is to be immediately introduced into the slide of the camera, in which it is to be exposed to the object for a few seconds (from 3 or 4 to 30 or 40), according to the nature of the object and the intensity of the light. The slide is then withdrawn from the camera, and the plate when examined will not be found to exhibit any image.

\* A suitable pyroxilin for this purpose may be obtained by taking a mixture of pure sulphuric acid, sp. gr. 1.833 at 60°, 10.4 fluid drachms, nitric acid, sp. gr. 1.448, 10.3 fluid drachms, water 1 fluid drachm—mix these liquids, and raise the temperature to 130° F., if necessary, by immersing the vessel in hot water. Immerse the paper in the acid (in the proportion of about 20 grains to the ounce) and let it remain in the acid for 20 or 30 minutes. Then press out the acid with a glass rod as completely as possible, and throw the pyroxilin into a large volume of cold water, and wash for half-an-hour; afterwards soak it well in water for some hours, lastly, wring it out in a cloth, and dry at a heat not exceeding 100° F. The substance thus obtained is completely soluble in a mixture of ether and alcohol. It is essential to attend to the strength of the acids and to the temperature employed. The proportions of acid are 2(HO, NO<sub>3</sub>) 4(HO, SO<sub>3</sub>) 7 aq. (Hadow, *Quart. Journ. Chem. Soc.*, vii. 201).



4. *Developing the Image.*—A latent image, however, exists, and it may be developed in the following manner:—Previous to commencing the operation, a developing liquid is prepared by dissolving 1 grain of pyrogallic acid, from 10 to 20 minims of glacial acetic acid, and 10 minims of alcohol, in an ounce of distilled water. Half an ounce or more of this liquid is then to be poured over the plate immediately after its removal from the camera. The negative image which is thus gradually developed, will be more intense if immediately before using the pyrogallic solution an addition be made to it of the same solution of nitrate of silver as is employed in the bath, in the proportion of 2 drops to each drachm of the developing liquid.

The exact reaction which occurs in this remarkable process is not known. The pyrogallic acid, however, is a substance which has a strong tendency to combine with oxygen, and under the conjoined action of iodide of silver and nitrate of silver (the presence of this salt in excess being necessary to the reaction) a portion of silver is reduced somewhat in the manner represented by the subjoined symbols, in which P represents pyrogallic acid.



Unless the plate has been exposed to light, the result would be such as is shown in No. 1, in which no action is represented as having occurred. In No. 2 the silver is represented as having been liberated upon the surface of the film of collodion, the quantity of iodide of silver remaining unaltered, but the iodine being transferred to a particle of silver previously in combination with nitric acid, whilst the nitric and pyrogallic acids react upon and destroy each other.

Other solutions may be employed for developing the latent image. One which answers very well for this purpose consists of,—crystallized sulphate of iron from 12 to 20 grains, glacial acetic acid 20 minims, alcohol 10 minims, and water 1 ounce. It is not, however, so well adapted for the production of deep shadows as the pyrogallic acid. When the picture is sufficiently distinct, it must be washed with clean water, and fixed by immersing it in a solution of hyposulphite of soda till the cream-coloured iodide of silver is entirely removed. A solution of cyanide of potassium, containing from 2 to 12 grains of the salt in an ounce of water, may be substituted for the hyposulphite of soda for the purpose of fixing the image. The picture is again to be thoroughly washed in clean water; it is allowed to dry, then heated before a fire until the fingers can but just

bear to touch the glass, and the film is protected from mechanical injury by covering it with a coat of transparent spirit varnish by a manipulation similar to that employed in coating the plate with collodion. This varnished photograph may then be employed for procuring positive pictures by means of the sensitive paper prepared with chloride of silver upon Mr. Talbot's plan (882). By the addition of a certain proportion of iodide of iron, and by other means, the sensitiveness of the collodion film to the action of light may be so highly exalted, that moving objects, such as the waves of the sea, or a crowd of people, may be successfully depicted by the instantaneous action of light upon the plate.

(885) *Albuminized Plates*.—M. Niepce de St. Victor introduced the employment of glasses coated with albumen, obtained by beating up whites of eggs with 1 per cent. of iodide of potassium: the liquid is to be placed for 12 or 24 hours in deep vessels, to become clear, after which the supernatant liquid is to be poured upon glass so as to produce a uniform layer; it is then allowed to dry for 12 hours, and is fit for the bath of nitrate of silver. Albuminized glasses may be preserved for some weeks without injury; they may be excited by means of Talbot's mixture of acetate of silver with gallic acid (883). The image is developed by means of a solution of gallic acid, after the plate has been exposed in the camera.

(886) *Photographic Engraving and Lithography*.—In the year 1827, M. Niepce published a process for obtaining pictures by the aid of light, the basis of which was the fact that the bitumen of Judea, when exposed to the sun's rays, becomes insoluble in oil of lavender, whilst those parts which have remained in shadow preserve their solubility. This process has, with some modification, been applied by M. Niepce de St. Victor, the nephew of the inventor, to the production of engravings upon steel. Powdered asphalt and a small proportion of pure beeswax are dissolved in oil of lavender, and then mixed with an equal volume of benzole. The surface of the steel plate which is to be engraved is first carefully cleaned with whiting and water, after which a solution of hydrochloric acid in 20 parts of water is poured over it, and the plate is immediately washed and dried. The solution of bitumen is then poured upon the plate in a darkened chamber, and dried by the application of a gentle heat. A good *positive* photographic proof is now applied to the surface, covered with glass, and exposed for a short time to the action of diffused light. The exposed plate is next subjected to the action of a mixture of 3 parts of rectified naphtha and 1 of benzole; the parts which have not

been exposed to light are gradually acted upon by this mixture. When the process of solution has proceeded far enough, the solvent is washed off with water, and the exposed parts of the plate are 'bitten in' with a mixture of 1 measure of nitric acid, sp. gr. 1.33, 2 measures of alcohol, sp. gr. 0.844, and 8 measures of water. The plate is then submitted to the ordinary processes employed in aquatint engraving.

A modification of this process has been applied to the purposes of lithography. In this case the bitumen is dissolved in ether, and poured upon a properly prepared lithographic stone; a negative photograph is then placed upon it, and exposed to the light. The plate is next washed with ether, which dissolves the unexposed parts of the film, leaving those which have been acted on by light. The stone is then treated with dilute acid, and thoroughly washed, after which it may be used for printing with ordinary lithographic ink, which attaches itself to the parts upon which the bitumen is left. The process is said to give excellent results (Delouze and Frémy, *Trailé*, iii. 477).

(887) *Chrysotype*.—Other processes more or less analogous to the Talbotype have been contrived: one of them was invented by Sir John Herschel, and described by him under the name of the *chrysotype* (*Phil. Trans.*, 1842, pp. 206, 209). Paper is washed over evenly with a solution of ammonio-citrate of iron, of such a strength as when dry to produce a good yellow colour. It is placed in sunshine in a camera, or under any engraving which it may be intended to copy; after a few minutes' exposure it is to be removed, and instantly washed over with a neutral solution of chloride of gold; a positive picture is thus developed, which assumes great sharpness, becoming gradually deeper up to a certain point; at the instant when it ceases to gain in intensity (this point being easily seized by practice), the picture is put into pure water, and rinsed thoroughly in order to remove the excess of solution of gold; it is then fixed with a solution of iodide of potassium, and again washed to remove the superfluous salts.

In this case the persalt of iron, under the influence of the organic matter of the paper, becomes partially reduced to a salt of the protoxide, in the parts exposed to light; and this proto-salt of iron, when washed over with the solution of gold, precipitates this metal in the reduced state, and thus gives rise to the coloured image. Water, by removing the excess of the salts, fixes the picture and prevents it from experiencing further change on exposure to light.

(888) *Daguerreotype*.—In the year 1839, M<sup>r</sup> Daguerre made

known his beautiful method of obtaining photographic pictures upon metallic plates. The essential parts of this process are as follows:—A sensitive film of the iodide of silver upon a silver plate is exposed to the action of light in the camera. The latent image is then developed by exposure to the vapour of mercury, after which the picture is fixed by means of hyposulphite of soda.

1. *Polishing the Plate.*—For this purpose, a polished sheet of plated copper is taken, and cleaned by rubbing it over first with finely powdered tripoli on a pledget of cotton moistened with a few drops of alcohol, and afterwards with dry cotton, until when breathed upon the metal assumes a uniform dull surface, from which the cloud disappears without showing any patches or spots; after this the plate is carefully polished, by means of a long polishing board faced with buckskin. If this preliminary operation be not carefully performed, the subsequent steps will not lead to any satisfactory result; the touch of a finger upon the polished surface is sufficient to soil it.

2. *Iodizing.*—The plate is next exposed for a few minutes to the vapour of iodine, till a thin yellow film is produced uniformly over the surface. This operation should be performed by candle-light, or in a room furnished with a window supplied with yellow glass; the plate must be protected from diffused daylight.

3. *Exposure.*—If such a plate be exposed for a few minutes in the focus of a double achromatic lens, adjusted to a camera obscura in such a manner that the image of the object to be copied shall fall upon the iodized surface, it undergoes an alteration which, however, is not perceptible on withdrawing the plate from the camera.

4. *Development.*—But if the plate be exposed for a few minutes to the vapour of mercury, heated to about  $140^{\circ}$  F., the latent image gradually appears, with all the shadows, lights, and half tints faithfully reproduced. Much of the success depends upon the proper length of exposure to the action of light, and in this respect practice is the best guide; if too short a time be allowed, the picture is dark and indistinct; if the light has acted too powerfully, the shadows become metallic in appearance, and ill defined; and if the action be continued for a sufficient length of time, the picture becomes reversed, or *negative*, the shadows in such a case being represented by lights, and the lights by shadows. A due exposure to the mercurial vapours constitutes an important part of the operation; for if this exposure be insufficient, the whites have a bluish cast, and if it be too long continued, the blacks become indistinct and misty.

Mr. Goddard, in the year 1841, discovered that the iodized plate

may be rendered very much more sensitive to the action of light, by exposing it for a few seconds to the vapour of bromine, or of chloride of bromine, so as to obtain a mixed film of iodide and bromide of silver, or of iodide, chloride, and bromide of silver. The process thus was rendered applicable to portraits, and the operation could be accomplished in as many seconds as it before required minutes. The usual practice now is, after having obtained an orange-coloured film by exposure of the silver plate to the vapour of iodine, to expose it to the fumes of bromine from bromide of lime, until the film assumes a rose colour; after which it is a second time returned to the iodine box, for a period equal to one third of that occupied by the first iodizing. The plate is then exposed in the camera; after which it is mercurialized.

In order to fix these pictures, Daguerre employed a solution of hyposulphite of soda, and then washed the plates with water. The effect of the Daguerreotype may be much improved by gilding them by the process of M. Fizeau; they are thus rendered less liable to mechanical injury, and a richer and warmer effect is given to the impression:—for this purpose, 1 part of neutral chloride of gold and 3 parts of hyposulphite of soda may be dissolved in 500 parts of water; the plate having been placed in a horizontal position, is to be completely covered with a small quantity of this liquid, and the plate is heated by a large spirit-lamp flame until small bubbles appear on its surface. All traces of iodide of silver are thus removed, and the surface of the plate becomes coated with a thin film of reduced gold. It must then be washed with distilled water, drained, and dried by the application of a gentle heat to the back of the plate.

The following theory may be offered in explanation of the changes which occur during the production of the Daguerreotype image. Under the influence of light the superficial layer of iodide of silver is modified so as to render it susceptible of decomposition. When the plate is acted upon by the mercurial vapour, the iodine is driven to the deeper layer of silver, and a film of silver is liberated upon the surface of those parts which have been exposed to the action of light, the thickness of this film varying with the intensity and duration of the light. The reduced silver combines with the mercury, and a film of silver amalgam is formed, varying in thickness with the thickness of the silver film; in consequence of which the reflected tints differ according to the varying thickness of this film: those parts of the iodized plate which have not been exposed to the light, of course do not com-

bine with the mercury. After the plate has been treated with hyposulphite of soda, the excess of iodide of silver is removed, and the blacks consist of metallic silver. Experiment proves that those parts of the plate immediately beneath the highest lights, are more deeply corroded than the others, by the action of the iodine, which has been driven inwards during the process of mercurialization.

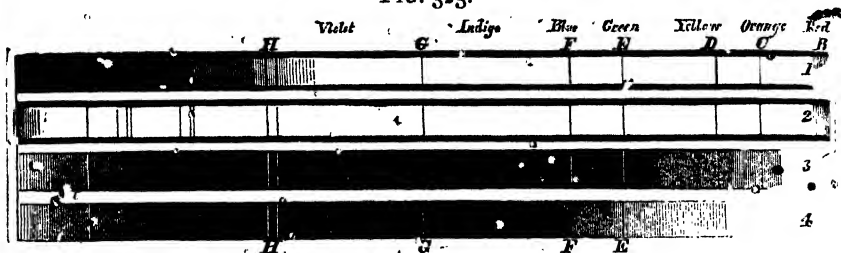
In complete accordance with the foregoing explanation, is a curious fact first pointed out by Mr. Shaw, that if a plate after it has received the impression in the camera, but before it has been mercurialized, be exposed to the vapour of iodine or bromine for a few seconds, the image is completely effaced, and is no longer producible by mercury.

The surface of the plate is rendered uneven by the operation of light upon it, so that it admits of being copied by the process of electrotyping (874). Impressions on paper have been printed from an etched Daguerreotype plate, the biting-in being produced by dilute nitric acid, which attacks the shadows (the reduced silver), and leaves the lights (the amalgam) untouched.

(889) *Action of the Solar Spectrum on Photographic Bodies.*—If a pure solar spectrum be allowed to fall upon a sheet of sensitive paper, prepared by washing it over first with common salt, and then with nitrate of silver, it will be speedily apparent that the chemical action is not uniformly distributed over the luminous image. The maximum of light falls in the yellow rays about Fraunhofer's line *D* (fig. 323), whilst the maximum of chemical action occurs in the blue portion of the spectrum, near the line *G*, about one-third of the distance between it and the line *H*. The blackening effect generally extends as far as *r* in the green, whilst it is prolonged beyond the violet end of the spectrum to a distance nearly equal to two-thirds of the length of the luminous spectrum, the chemical effect gradually shading off until it comes imperceptible; the maximum point of action, however, varies with the preparation which is used. When the Talbotype iodized paper is employed, the maximum blackening is found on the extreme limit of the violet rays. Where the bromide of silver forms the sensitive material, the chemical action is prolonged into the red ray, and the greater part of the impression is of a uniform grey-black. When paper washed with chloride of gold is employed as the sensitive surface, the maximum effect is produced between the green and the blue rays, and the chemical action does not extend beyond the violet extremity for more than half the distance over which these effects are

produced upon the salts of silver. In fig. 323, 1 represents the space occupied by the luminous spectrum on white paper; 2, the same spectrum thrown on a fluorescent screen, viz., turmeric paper, by

FIG. 323.



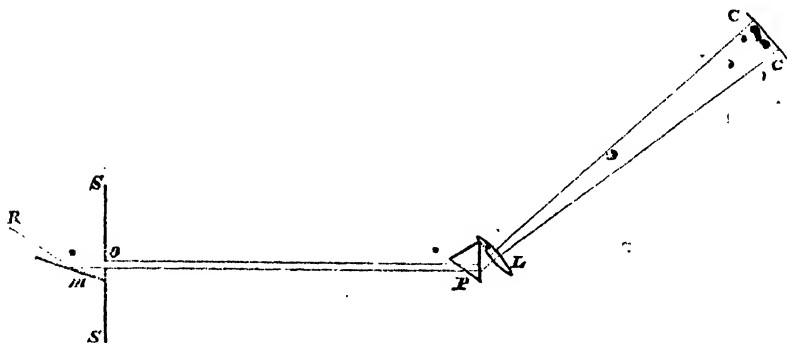
which it is rendered visible almost to the extreme limit of chemical action; 3, the chemical spectrum on bromide of silver; 4, the Talbotype spectrum. Sir John Herschel, Mr. Hunt, and M. E. Becquerel have succeeded more or less perfectly in obtaining coloured impressions of the spectrum upon chloride of silver, but they have been unable to fix them. Sir J. Herschel (*Phil. Trans.* 1840), says that the impression "was found to be coloured with sombre but unequivocal tints, imitating those of the spectrum itself." The coloration commenced in the orange rays. M. Becquerel appears to have obtained more brilliant colours by employing a plate of silver which had been superficially converted into chloride by immersing it in dilute hydrochloric acid, and by making it the positive plate of a voltaic battery.

Inactive spaces occur in the chemical spectrum, which correspond exactly with those which are found in the visible spectrum, but they extend also into the prolongation beyond the violet extremity, and occur there in great number. These fixed lines may be obtained upon Talbotype paper, or, still better, upon a surface of collodion, in the following manner:—

Let *s s*, fig. 324, represent a shutter of a room which can be rendered completely dark; *o* is an opening or slit of about  $\frac{1}{4}$ th of an inch wide, through which a beam of solar light is reflected by a heliostat *m*, or from a mirror, the angle of which to the ray admits of regulation from within the room; *L* is a lens of from 20 to 30 inches focal length; *P*, a prism;—the lens and prism may be made of glass free from striæ, but they are best constructed of rock crystal: the distance of *L* from the aperture is equal to twice its focal length. If the prism be placed so as to produce the minimum deviation of the ray, and as close to the lens as can be, at *c c*, which is at as great a distance behind the lens *L* as *o* is in front

of it, a spectral image of the aperture will be formed, and may be received upon a screen. All the coarser lines of the visible spectrum may be traced by the unaided eye, when the spectrum is received on a screen of white paper; and if a sheet of turmeric paper be used, many of the lines beyond the violet are also rendered visible: by substituting a sensitive surface, such as collodion, for the screen of white paper, a faithful copy of these lines may be obtained.

Fig. 324.



It is remarkable that the chemical rays appear to be identical with those which produce *fluorescence*, as the phenomenon investigated by Professor Stokes (104) has been termed. If the solar rays be transmitted through a layer of a concentrated but colourless solution of sulphate of quinine, no extra-spectral prolongation of chemical action is produced when this light is allowed to fall upon a sensitive surface. By varying the source of light, the chemical powers of the spectrum are varied also. The chemical action of the flame of the hydrocarbons, however intense the light, is but feeble; that of the lime light is much more marked, while that of the electric light between charcoal points greatly surpasses either; and these results coincide exactly with their relative power of exciting the phenomena of fluorescence.

(890) It was stated 50 years ago by Ritter, and the observation has been confirmed and extended by Sir J. Herschel, that the two ends of the spectrum produce opposite chemical effects, though the violet appears greatly to predominate in power. If, for example, paper soaked in nitrate of silver be partially blackened by exposure to diffused daylight, and then submitted to the action of the solar spectrum, the portion upon which the violet end falls speedily becomes much darker, while the portion beneath the red rays assumes a brick-red hue. If the spectrum be thrown upon white nitrated paper, and diffused daylight be allowed at the same



time to fall upon it, the spot where the red rays fall retains its whiteness while the rest of the paper speedily darkens. It thus appears, that by combining the influence of two rays of different refrangibilities, effects are producible which cannot be obtained by either ray separately.

Blackened nitrate paper, if washed over with a solution of iodide of potassium, becomes gradually bleached when exposed to diffused daylight. If the solar spectrum be allowed to fall upon paper thus prepared, whilst moist, and before it has become bleached, the part beneath the violet end is quickly bleached; but this effect is bounded by a sharp border in the yellow, while the paper under the red end becomes darker.

Mr. Claudet (*Phil. Transactions*, 1847) found that an iodized Daguerreotype plate, when submitted in the focus of a camera to the red image of the sun as seen through a London fog, became subsequently whitened on exposure to the vapour of mercury, in all parts, excepting in the track traversed by the image of the sun—this portion continued perfectly black. In another experiment, a plate was covered with black lace, and exposed to diffused daylight; after a few minutes' exposure, one half of the plate was covered with an opaque screen, the other half with a red glass, and the exposure was continued for a short time: in the mercury box the red half continued black, whilst, on the other portion, the image of the lace was distinctly traced. The photographic effect at first produced over the whole plate had in fact been neutralized by the red glass.\* A pleasing variation of the last experiment was made by exposing an iodized plate to diffused daylight, then covering it with a piece of black lace, and screening it with a red glass; a negative picture was now developed in the mercury box, the red glass having destroyed all photographic action except on those parts screened by the lace. Orange and yellow glasses give similar results. After exposing a plate to daylight, and then submitting it to the action of red glass, it again becomes sensitive to light, so that, as M. Claudet observes, it is no longer needful to prepare the plates in a dark chamber, as, if placed beneath a covering of red glass, they are always ready for immediate use,—even though subsequently to

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\* It must be borne in mind that all results obtained by coloured media are liable to ambiguity, as it seldom happens that the light transmitted through them is homogeneous (102); the effects are liable to become complicated from the intermixture of results produced by rays from different parts of the spectrum.

their preparation they may have been for some time exposed to solar light.

But though the red and yellow glass have the power of completely counteracting the effect of the radiation of the more refrangible rays, they have a peculiar effect of their own. The neutralizing power of the red ray is exerted more slowly than the photographic effect of the white light, nearly in the proportion of 100 to 1; that of the yellow ray was found to be about 10 to 1.

From the foregoing remarks it is evident that the colour of objects must exert a material influence upon the nature of the photographic images produced. Reds and yellows, from the want of chemical energy in this portion of the ray, will be characterized by absence of photographic action in the image, and will be represented by black spots, which often produce singular disfigurement in portraits. Yellow freckles, for instance, on the skin of the face are accurately copied, but are depicted in the portrait as black spots. Much judgment and knowledge is therefore required in selecting a dress of a colour which is adapted to produce a suitable depth and contrast of tint in the photograph.

(891) *Action of the Solar Spectrum on Vegetable Colours.*—This subject has been particularly examined by Sir J. Herschel (*Phil. Trans.*, 1842). White paper coloured with various vegetable juices was subjected by him to the influence of the prismatic spectrum, and in some cases these papers were washed over with solutions of metallic salts. The following are the most important general conclusions which may be drawn from these experiments:—1. That the action of light is in almost all cases of a nature to obliterate the colour; or if it does not entirely bleach it, a faint residual tint is left, upon which it has little further action. The older the paper or the tincture, the more decided is this residual tint, which is probably the result of an oxidizing action upon the colouring material, independent of the action of light. 2. The action is confined to the luminous rays of the spectrum,—offering in this respect a marked difference between these actions and those produced upon the metallic compounds. 3. The rays which are most effective in destroying a given tint are in many cases those which are complementary (102) to the tint destroyed. Orange-yellows, for instance, are bleached most powerfully by the blue rays: blues by the red, orange, and yellow rays; and purples and pinks by the yellow and green rays.

## CHAPTER XIX.

ON THE DETERMINATION OF THE EQUIVALENT NUMBERS OF THE  
ELEMENTARY BODIES.

(892) *Aid derived from Analysis in Fixing the Equivalent of a Body.*—The determination of the equivalent number of a body is an operation of great delicacy, and often involves many very difficult questions. The first object which the chemist has in view is to select some substance the composition of which is tolerably simple, which can readily be procured in a state of purity, and to determine the proportions of each of its components in 100 parts of it. It is of great importance that the operations by which these results are obtained should be as few in number, and as simple and manageable as possible. It is not, however, sufficient that three or four different experiments conducted in the same manner should give uniform results: the mode of analysis adopted should, if possible, be varied so as to escape any unperceived source of error which depends upon the process employed. It is also desirable to vary the compound upon which the analysis is made. Thus, the equivalent of a metal may in some instances be ascertained by fixing the proportion of oxygen which a given weight of the metal requires for its conversion into the state of oxide; in other cases, by decomposing a known weight of the pure oxide in a current of hydrogen, the proportion of oxygen and of metal can be determined very exactly by ascertaining the loss of weight which the oxide experiences. It is, however, advisable to check these results, not only by trials upon different quantities of the metals, or of the oxide prepared at different times, but also (in order to guard against the occurrence of any unperceived impurity in the substance under experiment) to ascertain if the analysis of the chloride, the sulphide, or some other compound of the metal, gives a similar numerical value for its combining proportion.

(893) *Aid derived from Isomorphism, Specific Heat, and Combining Volume of Vapour.*—The determination of the chemical equivalent of an element, however, does not rest simply upon the knowledge of the proportion in which it enters into combination with a given amount of oxygen or of any other simple body. When a substance forms but a single combination with oxygen, the simplest hypothesis is that the compound so formed consists of a single equiva-

ment of each of its components. Thus magnesium and zinc each form but a single oxide, and they are assumed to be protoxides, or oxides containing 1 equivalent of the metal to 1 equivalent of oxygen. Such oxides neutralize a quantity of nitric acid which contains five times as much oxygen as the base. But it not unfrequently happens that the same metal forms two oxides, in one of which a given weight of oxygen combines with twice as large a proportion of the metal as in the other: for example, 8 parts of oxygen unite with either 31.75 of copper to form the black oxide, or with 63.5 of the metal to form the red oxide, and both oxides can combine with acids. In like manner, 8 parts of oxygen form with mercury two salifiable oxides, one containing 100, the other 200 of mercury. The question to be determined then is, which of these numbers is to be regarded as the equivalent of the metal? In cases of this kind, the judgment requires aid from analogy, or from collateral circumstances, such as the isomorphism of the bodies when compared with others of known composition; the circumstance that the specific heat of the body, when multiplied into its supposed equivalent, yields the same product as that obtained by multiplying the specific heat of some other element into its admitted equivalent number; or the formation of a volume of vapour from the supposed equivalent, which is equal in bulk to the volume of an equivalent of hydrogen. Such assistance is afforded in the case of copper by the isomorphism of the compounds of the black oxide of this metal with corresponding compounds of zinc and magnesia. If zinc be a protoxide, the black oxide of copper is also a protoxide, and the red oxide must be considered as a suboxide. Another character of some importance, but subordinate to that of isomorphism, is afforded by the specific heat of the metal. Assuming zinc to be a protoxide, its equivalent number is 32.5, and its specific heat is found to be 0.0955; the product of these two numbers is 3.103. The specific heat of copper is 0.0951, and assuming the black oxide to be the protoxide, its equivalent is 31.75; the product of these two numbers is 3.019, or nearly the same as in the case of zinc; whereas, if the red oxide were assumed to be the protoxide, it would be double this number.\*

\* If, however, this consideration were allowed to be decisive, it would be necessary to modify the numbers generally received for several of the elements. The equivalents of bromine, of iodine, of phosphorus, of arsenic, of antimony, of silver, and of gold, would require to be reduced by one half.

In the determination of the equivalent of mercury, assistance may be derived from another character; since as it is a volatile metal it can be converted into vapour, and the density of that vapour can be ascertained. Now the specific gravity of the vapour of mercury is 6.976, and that of hydrogen is 0.0694; or allowing for unavoidable errors of experiment, the density of mercurial vapour is 100 times as great as that of hydrogen. An equivalent of hydrogen = 1 gives a volume of vapour which occupies double the space of that required by an equivalent of oxygen. If 100 be assumed as the equivalent of mercury, it yields a volume of vapour equal to that of an equivalent of hydrogen, or double that of oxygen; whereas, if 200 be the equivalent of mercury, 1 equivalent would yield 4 times the volume of vapour afforded by an equivalent of oxygen, which would be highly improbable, as no other element possesses any similar vapour volume.

It is not safe, however, to assume in cases in which only one compound exists between an element and oxygen, that such compound is necessarily a protoxide; aluminum is not known to form more than a single oxide, yet chemists do not hesitate to consider this oxide as a sesquioxide, and in this judgment they are guided by analogy:—Thus, those bodies which are admitted to be protoxides are generally powerful bases, and neutralize the acids very completely; now alumina does not present this character; its salts have a powerful acid reaction and taste. But the arguments of most weight against the supposition that alumina is a protoxide, are derived from the composition and properties of the oxides of iron. Iron forms two basic oxides: one contains but two-thirds of the proportion of oxygen which is present in the other. The oxide of iron with the smaller proportion of oxygen is a powerful base, and forms salts with acids which are isomorphous with those of magnesia and zinc. It is consequently regarded as a protoxide, and the other oxide is looked upon as a sesquioxide; the basic properties of the latter are much more feeble, and the salts which it forms with acids have, like the salts of alumina, a powerful acid reaction. Sesquioxide of iron, moreover, is isomorphous with alumina when in combination. An iron alum may be obtained in octohedral crystals, in which the place of the aluminum is supplied by that of iron: and native peroxide of iron is found in forms of the rhombohedral system isomorphous with native alumina in corundum. Hence, if the red oxide of iron be a sesquioxide, alumina must be a sesquioxide also.

An excellent illustration of the value of isomorphism in these cases is also afforded by the oxides of chrome. Until the publication of Peligot's researches on this metal, only two compounds of chrome with oxygen were known, viz., the green oxide and chromic acid; the acid containing twice as much oxygen as the oxide. In these two compounds the proportion of oxygen combined with the equal weights of chromium was as 1 : 2, or as  $1\frac{1}{2}$  : 3. But there was little difficulty in deciding that the green oxide must be regarded as a sesquioxide, for the green oxide of chromium was known to be isomorphous with the red oxide of iron, both in its uncombined form, and when in combination with the same acids. Chromic acid would, therefore, contain 3 equivalents of oxygen to 1 of the metal. But evidence still more conclusive of the accuracy of this view is afforded by the fact that chromic acid is isomorphous with manganic acid; the latter is known to contain 3 equivalents of oxygen, as it is the acid of a metal which yields an oxide with a given weight of manganese containing one-third of the oxygen present in manganic acid, and which, moreover, is isomorphous with the protoxide of iron. Finally, Peligot's discovery of another oxide of chromium, with a smaller proportion of oxygen than either of the compounds previously known, fully vindicated the correctness of the foregoing deductions; for Peligot's new oxide was found to contain one-third of the proportion of oxygen present in chromic acid. It also yielded salts isomorphous with the corresponding salts of the protoxide of iron, and the proportion of oxygen which it contained bore the same relation to that present in the green oxide of chrome that the oxide in the protoxide of iron did to that in the red oxide of iron. Peligot's new oxide therefore was the missing protoxide of chromium.

(894) *Numerical data from which the Equivalents of the Elements have been calculated.*

The following are the data upon which the equivalent numbers of the more important elementary bodies, given at page 17, have been determined:—

1. *Aluminum*.—Berzelius found that 100 parts of the tersulphate of alumina ( $\text{Al}_2\text{O}_3, 3 \text{SO}_3$ ) lost by intense ignition 70.056 of sulphuric acid; hence, assuming the equivalent of sulphuric acid as 40, that of aluminum (hydrogen being = 1) is 13.672, or, if oxygen = 100, it is 170.9.

2. *Antimony*.—100 parts of metallic antimony, when oxidized by nitric acid, yield 124·8 of antimonious acid ( $\text{SbO}_3$ ,  $\text{SbO}_5$ ); hence its equivalent ( $\text{H}=1$ ) is 129·02 or ( $\text{O}=100$ ), 168·29 (Berzelius).

3. *Arsenic*.—Pelouze decomposed a given weight of chloride of arsenic by means of water, and determined the quantity of chloride of silver which it produced; a mean of three experiments gave 75, or 937·5 as the equivalent of arsenic.

4. *Barium*.—Berzelius found that 100 parts of chloride of barium when dissolved in water yielded 112·175 of sulphate of baryta, on the addition of sulphuric acid; and that 100 parts of the chloride when mixed with solution of nitrate of silver yielded 138·87 of chloride of silver. Pelouze, by precipitation with silver, obtained results almost identical: the number given by Berzelius is 68·42; that by Pelouze is 68·64, or 858·03.

5. *Bismuth*.—100 parts of the metal converted into nitrate, and decomposed by heat in a glass vessel, gave 111·275 of oxide,  $\text{Bi}_2\text{O}_3$ ; hence its equivalent is 212·86, or 2660·75 (Lagerhjelm).

6. *Boron*.—According to Berzelius, 100 parts of borax lost 47·1 of water, and yielded 16·31 of soda, leaving for boracic acid (by difference) 36·59; and Davy found by the direct combustion of boron, that 100 parts of boracic acid contain 32 of boron and 68 of oxygen. This would make the equivalent of boron 10·9, or 136·2. But the methods which were employed are admitted by Berzelius not to be such as to warrant entire confidence in the accuracy of this number.

7. *Bromine*.—Marignac found that 3·946 grammes of silver, when dissolved in nitric acid, required 4·353 grammes of bromide of potassium for its complete precipitation, and 15·00 of silver converted into nitrate gave 26·11 of bromide of silver; taking the equivalent of silver at 107·97, a mean of the experiments gives the equivalent of bromine as 79·97, or 999·62. It may without sensible error be taken as 80.

8. *Cadmium*.—Stromeyer found that 114·352 parts of the oxide yielded 14·352 of oxygen; from which the equivalent of this metal is 55·74 or 696·767.

9. *Calcium*.—Dumas, by the ignition of 100 parts of Iceland spar, obtained 56 parts of lime, which would make the equivalent of calcium exactly 20. Erdmann and Marchand estimate it at 20·03; Marignac, by decomposition of a known weight of the chloride of calcium, estimated it at 20·105; and Berzelius, by the

conversion of a known weight of pure lime into sulphate, found it to be 20.13 or 251.65.

• 10. *Carbon*.—The determination of the equivalent of carbon formed the subject of a laborious series of researches by Dumas and Stas. They burned graphite, diamond, and charcoal, in a current of pure oxygen with scrupulous care. 1.375 grammes of diamond gave 5.041 of carbonic acid: and the mean of their results, which agreed very closely with each other, fixed the equivalent of carbon at 6.0 or 75. Similar experiments by Erdmann, and Marchand gave them as a result, 6.007; and the results obtained by Liebig and Redtenbacher coincide very nearly with the foregoing.

11. *Chlorine*.—Numerous careful experiments have been made with a view to determine the equivalent of chlorine. Marignac found that 100 parts of chlorate of potash, when decomposed by heat, left 60.839 of chloride of potassium; and 22.032 of pure silver required 15.216 of chloride of potassium for its complete precipitation. 14.427 of chloride of potassium gave 27.749 of chloride of silver. Berzelius calculates from these results that the equivalent of chlorine is 35.46. Maumené, by heating chloride of silver in a current of hydrogen, found that 100 parts of silver were united with 32.856 of chlorine. The same chemist obtained from 100 parts of chlorate of potash 60.791 of chloride of potassium: and from 100 parts of chloride of potassium, he obtained by precipitation 192.75 of chloride of silver.

These experiments furnish data from which the equivalents of potassium and of silver may be determined, as well as that of chlorine, in the manner following:—

The composition of chlorate of potash is represented by the formula  $\text{KO}, \text{ClO}_6$ ; when heated it gives off the whole of its 6 equivalents of oxygen. The equivalent of chloride of potassium therefore will be the quantity which is combined with 48, or 6 equivalents of oxygen. Now, taking Maumené's result that 39.209 parts of oxygen are combined in chlorate of potash with 60.791 of chloride of potassium, we have—

$$39.209 : 48 :: 60.791 : x (=74.4208, 1 \text{ eq. of KCl})$$

If 100 parts of chloride of potassium produce 192.75 of chloride of silver, 1 equivalent or 74.4208 of chloride of potassium will furnish 1 equivalent of chloride of silver. Thus—

$$100 : 192.75 :: 74.4208 : x (=143.446, 1 \text{ eq. of AgCl})$$



and 132.856 of chloride of silver contain 32.856 of chlorine; consequently (1 equivalent of chloride of silver containing 1 equivalent of chlorine), we find the equivalent of chlorine as follows:—

$$132.856 : 32.856 :: 143.446 : x (=35.476):$$

but the equivalent of chloride of silver being  $=143.446$   
that of silver is found by deducting the equivalent of Cl  $= 35.476$

leaving the equivalent of silver  $=107.970$

and the equivalent of chloride of potassium being  $=74.4208$   
deduct from it the equivalent of chlorine  $=35.476$

we obtain the equivalent of potassium  $=38.9448$

No material error can therefore arise if the equivalent of chlorine be taken as  $= 35.5$  or  $443.75$

the equivalent of silver as  $=108.0$  or  $1250.0$

and the equivalent of potassium as  $= 39.0$  or  $487.5$

12. *Chromium*.—The equivalent of chromium was determined by Berlin, by converting chromate of silver into the chloride; the number thus obtained was 26.347. And that deduced from the reduction of the chromic acid to the sesquioxide of chrome, in the same series of experiments, was 26.27, or 328.38.

13. *Cobalt*.—Rothoff found that 269.2 parts of the protoxide of cobalt converted into protochloride by means of hydrochloric acid and precipitated by means of nitrate of silver, gave 1029.9 of chloride of silver: hence, if the cobalt be in the form of protoxide, the equivalent of cobalt is 29.49, or 368.65.

14. *Copper*.—Berzelius obtained from 7.68075 grammes of oxide of copper, which were reduced in a current of hydrogen, 6.13075 of metallic copper; hence the equivalent of the metal is 31.75, or 395.69. Erdmann and Marchand, by a similar method, fixed it at 31.76.

15. *Fluorine*.—Berzelius found that 100 parts of fluor spar, when heated with an excess of sulphuric acid, yielded 175 of sulphate of lime. Louyet, on repeating this experiment, obtained 174.361 parts of sulphate of lime. The equivalent of fluorine, deduced from this latter result is 19, or 237.5.

16. *Gold*.—Berzelius, by reducing the double chloride of gold and potassium in a current of hydrogen, determined this equivalent at 196.66, or 2458.33. By an earlier series of experiments, he found that 142.9 of metallic mercury precipitated 93.55 of gold from the tetrachloride; 3 equivalents of mercury causing the preci-

precipitation of 2 equivalents of gold, and assuming the equivalent of mercury to be 100, this would make the equivalent of gold 196.44. This number is double that given at p. 17.

17. *Hydrogen*.—The equivalent of hydrogen was determined with great care by Dumas, by the method already described at p. 470. He ascertained, as a mean of nineteen experiments, that 8 parts of oxygen combined with 1.0012 of hydrogen to form water; the lowest quantity which these experiments gave being 0.9984, the highest 1.0045. The quantity of water collected in each of these experiments was considerable, varying from 230 to 1100 grains. Erdmann and Marchand repeated these experiments with similar results. Berzelius and Dulong concluded, from researches performed long previously upon a similar principle, though on a smaller scale, that the quantity of hydrogen united with 8 parts of oxygen was 0.9984, which coincides with the lowest number obtained by Dumas. It is obvious that no appreciable error can be committed by assuming hydrogen to possess an equivalent of 1, that of oxygen being 8, or 12.5, if oxygen be taken at 100.

18. *Iodine*.—Marignac determined this equivalent by a process analogous to that which he employed for chlorine. The equivalent of iodide of potassium he fixed at 165.951; deducting from this 38.944, the equivalent of potassium, we obtain 127 as the equivalent of iodine, or 1587.5.

19. *Iron*.—Berzelius found that 1.586 grammes of pure iron converted first into nitrate, and then into sesquioxide by ignition, gave 2.265 of sesquioxide; and Svanberg and Norlin, by reducing sesquioxide of iron in a current of hydrogen, obtained from 35.783 of sesquioxide, 25.059 of metallic iron; making the equivalent of iron 28.04, or 350.5. Erdmann and Marchand, by the method last named, fixed the equivalent at 28.001, and Maumené has also arrived at a similar result by the oxidation of iron by aqua regia, and precipitating the oxide by means of ammonia.

20. *Lead*.—21.9425 grammes of oxide of lead were reduced by Berzelius in a current of hydrogen, and gave 20.3695 of metallic lead; as a mean of five experiments, he determined the equivalent of the metal at 1294.645, or 103.57. This result has been confirmed by Marignac.

21. *Magnesium*.—100 parts of magnesia dissolved in pure sulphuric acid and ignited, gave 293.985 of sulphate of magnesia; hence the equivalent of magnesium would be 12.65, or 158.14 (Berzelius).

Scherrer, by determining the quantity of sulphate of baryta produced by a given weight of sulphate of magnesia, determined the equivalent of magnesium at 12.11. Svanberg and Nordenfeldt, by the decomposition of the oxalate of magnesia ( $\text{MgO}$ ,  $\text{C}_2\text{O}_3$ , 2  $\text{HO}$ ) by heat, estimate it at 12.35; and by converting a known weight of magnesia into sulphate, found it to be 12.37; and Marchand and Scherrer, by ignition of the native carbonate, assign to it the number 12.02. The mean of these results is 12.16.

22. *Manganese*.—4.26775 of chloride of manganese gave Berzelius 9.575 of chloride of silver; the equivalent of the metal, from a mean of two such experiments is 27.57, or 344.684.

23. *Mercury*.—Erdmann and Marchand obtained from 118.3938 grammes of red oxide of mercury 109.6308 of mercury; a mean of five experiments give 100.1 or 1251.29 as the equivalent of the metal.

24. *Molybdenum*.—The equivalent number 47.69 given by Berzelius he regarded only as an approximation. Svanberg and Struve, from an extensive series of experiments upon this metal, considered that the most accurate results were obtained by roasting the bisulphide of molybdenum in air: as a mean of their experiments they conclude that 100 parts of the bisulphide yield 89.732 of molybdic acid; and hence, if the equivalent of sulphur be taken at 16, that of molybdic acid will be 46.06. Berlin, from the quantity of molybdic acid left by the salt ( $\text{H}_4\text{NO}$ , 2  $\text{MoO}_3$  +  $\text{H}_4\text{NO}$ , 3  $\text{MoO}_3$  + 3  $\text{HO}$ ), found the equivalent (from a mean of four experiments), to be 45.98. The mean of these results scarcely differs from 46.0 or 575.

25. *Nickel*.—Rothoff converted 188 parts of oxide of nickel into chloride, and obtained from it 718.2 of chloride of silver; the equivalent of nickel hence deduced is 29.54 or 369.333.

26. *Nitrogen*.—Marignac, by converting 200 grammes of silver into nitrate, obtained 314.894 of the salt; 14.110 of nitrate of silver required for precipitation 6.193 of chloride of potassium; 10.339 of silver converted into nitrate required 5.120 of chloride of ammonium for complete precipitation; the mean result, as calculated by Berzelius, from several experiments performed in this manner gives 14.004 or 175.06, as the equivalent of nitrogen. Dr. Anderson, by the decomposition of nitrate of silver by heat, concluded that the equivalent of nitrogen was 13.95; and Svanberg, from the analysis of nitrate of lead, obtained the same result: the equivalent of nitrogen may therefore be taken as 14.

27. *Oxygen*.—The equivalent of oxygen is the standard to

which all others are referred; it is found to be a multiple by 8 of that of hydrogen.

28. *Phosphorus*.—According to Pelouze, a solution of 100 parts of silver in nitric acid are required to precipitate the chloride from 42.74 of trichloride of phosphorus; the equivalent, therefore, would be 32.02 or 400.3. Berzelius, from the silver reduced from sulphate of silver by a known weight of phosphorus, estimated the equivalent phosphorus at 31.36; and Schrötter concludes, from a mean of ten experiments, in which phosphorus was burned in a current of dry air, and thus converted into phosphoric acid, that the true equivalent is 31.

29. *Platinum*.—Berzelius found that 6981 grammes of the double chloride of platinum and potassium, when reduced in a current of hydrogen, gave 4.957 of a mixture of platinum and chloride of potassium; 2.822 of this was platinum: hence the equivalent of platinum is 98.56, or 1232.08.

30. *Potassium*.—Marignac's experiments on the chlorate of potash, related when speaking of the equivalent of chlorine, gave the equivalent of potassium, 39.1; those of Maumené, 39.95, and those of Pelouze, 39.14. It may therefore be taken as 39.

31. *Silicon*.—Berzelius found that 100 parts of silicon, when oxidized, yielded 208 parts of silica, and he calculates the equivalent at 22.222. Pelouze states that a solution of 3.685 parts of silver in nitric acid precipitated 1.454 of chloride of silicon, whence the equivalent would be 21.36, or 267. In the present work, however, the equivalent has been taken at two-thirds of this number, for reasons some of which are stated at page 611.

32. *Silver*.—This equivalent has been repeatedly determined with very great care. Marignac, by precipitation of a known weight of silver from its solution in nitric acid, as chloride, estimates the equivalent as 107.97; and the experiments of Pelouze and of Maumené agree almost exactly with this result; 108, or 1350, may therefore be taken as the equivalent of silver.

33. *Sodium*.—Berzelius found that 100 parts of chloride of sodium gave by precipitation 244.6 of chloride of silver; the equivalent of sodium would therefore be 23.17. Pelouze found, as a mean of three experiments, that 100 parts of silver required for precipitation 54.144 of chloride of sodium, whence the equivalent of sodium would be 22.97 or 287.17. It may be taken as 23.

34. *Sulphur*.—The equivalent of sulphur was estimated by Berzelius from the weight of sulphate of lead formed by oxidizing

a known weight of lead with nitric acid and heating it with an excess of sulphuric acid till the weight ceased to alter. As a mean of three experiments, 100 parts of lead yielded 146.45 of sulphate of lead; hence the equivalent of sulphur would be 16.064; this result was confirmed by converting chloride of silver into sulphide in a current of dry sulphuretted hydrogen. Erdmann and Marchand made the equivalent of sulphur exactly 16, or 200. Their process consisted in distilling cinnabar with copper turnings: 100 parts of cinnabar gave 86.213 of mercury as a mean of 2 experiments.

35. *Tin*.—100 parts of tin, when oxidized by nitric acid and ignited, were found by Berzelius to yield 127.2 parts of peroxide; from which the equivalent of tin would be 58.82, or 735.29. Mulder states that he obtained from 100 parts of this metal 127.56 of peroxide of tin, which would make as the equivalent of tin 58.05.

36. *Tungsten*.—The number 94.64 given by Berzelius was only an approximation to the true one for this metal. Schneider, on repeating the experiment of reducing tungstic acid in a current of hydrogen, found that 100 parts of the acid yielded 79.316 of the metal, and on oxidizing metallic tungsten, and reconvertng it into tungstic acid, he found 79.327 parts of metal in 100 of acid; the equivalent of tungsten from the mean of these results would be 92.06. Marchand, by similar experiments, fixed it at 92.05, or 1150.6. It may be taken as 92.

37. *Uranium*.—Some doubt exists as to the exact equivalent of this metal. Peligot estimates it at 750 ( $O=100$ ), Wertheim at 740.51, from the double acetate of soda and uranium; and Ebelmen at 742.87, from the oxalate; Ebelmen's number would give the equivalent on the hydrogen scale as 59.43.

38. *Zinc*.—M. Favre, from the analysis of the oxalate of zinc, and from the determination of the quantity of hydrogen which a given weight of zinc liberates during its solution in hydrochloric acid, fixed this equivalent at 33.0; and M. Jacquelin, by the decomposition of the nitrate, and of the sulphate of zinc by heat, obtained the number 33.12. The original number given by Berzelius for this metal was 32.25. Subsequently Erdmann prepared a pure oxide of zinc, mixed it with pure charcoal obtained from sugar, and distilled the zinc in a current of hydrogen; he then oxidized the metal by nitric acid, and converted it into oxide by ignition; the equivalent of zinc, taking a mean of 4 experiments conducted in this manner, was 32.52, or 406.59. Pelouze obtained the same number from the analysis of the lactate of zinc.

(895) *Table of Equivalent Numbers*.—We may here sum up the

foregoing results by stating that the following numbers may be taken for the purpose of calculation, as representing the equivalents of the elementary bodies on the hydrogen scale. They differ in some cases slightly from the numbers given at page 17:—

Aluminum . . . 13.7	Hydrogen . . . 1.0	Potassium . . . 39.0
Antimony . . . 129.0	Iodine . . . 127.0	Rhodium . . . 52.2
Arsenic . . . 75.0	Iridium . . . 98.6	Ruthenium . . . 52.0
Barium . . . 68.5	Iron . . . 28.0	Selenium . . . 39.6
Bismuth . . . 213.0	Lanthanum . . . 46.0	Silicon . . . 14.24
Boron . . . 10.9	Lead . . . 103.6	Silver . . . 108.0
Bromine . . . 80.0	Lithium . . . 6.5	Sodium . . . 23.0
Cadmium . . . 55.7	Magnesium . . . 12.16	Strontium . . . 43.8
Calcium . . . 20.0	Manganese . . . 27.6	Sulphur . . . 16.0
Carbon . . . 6.0	Mercury . . . 100.0	Tellurium . . . 64.0
Cerium . . . 46.0	Molybdenum . . . 46.0	Thorium . . . 59.5
Chlorine . . . 35.5	Nickel . . . 29.5	Tin . . . 58.8
Chromium . . . 26.3	Nitrogen . . . 14.0	Titanium . . . 24.2
Cobalt . . . 29.5	Osmium . . . 99.4	Tungsten . . . 92.0
Copper . . . 31.75	Oxygen . . . 8.0	Uranium . . . 60.0
Fluorine . . . 19.0	Palladium . . . 53.2	Vanadium . . . 68.5
Glucinum . . . 7.0	Phosphorus . . . 31.0	Zinc . . . 32.5
Gold . . . 196.6	Platinum . . . 98.6	Zirconium . . . 33.8

(896) *Gerhardt's Notation*.—M. Gerhardt, starting with the assumption that the equivalents of all compound bodies yield two volumes of vapour, has been induced to modify some of these numbers, and his example has been followed by Dr. Williamson and some other chemists. The equivalents of oxygen, carbon, sulphur, selenium, and tellurium remain the same as those commonly adopted; he divides those of nearly all the other elements by two; or if the reduced equivalent of hydrogen be adopted as the unit of comparison, the equivalent

of oxygen	= 16	of selenium	= 79.2
of carbon	= 12	of tellurium	= 128.0
of sulphur	= 32		

the other numbers remaining unaltered. In the inorganic division of the science comparatively little advantage is gained by this change; but in many instances, where organic compounds are considered, the method leads to a considerable simplification of the formulæ employed. A few formulæ are subjoined for the purpose of contrasting them with those in ordinary use:—

Compounds.	Ordinary Formulæ.	Gerhardt's Formulæ.
Water . . . . .	HO . . . . .	H <sub>2</sub> O.
Potash . . . . .	KO . . . . .	K <sub>2</sub> O.
Hydrate of Potash . . . . .	KO, HO . . . . .	KHO.
Oxide of Silver . . . . .	AgO . . . . .	Ag <sub>2</sub> O.
Hydrochloric Acid . . . . .	HCl . . . . .	HCl.
Chloride of Potassium . . . . .	KCl . . . . .	KCl.

Compounds.	Ordinary Formulæ.	Gerhardt's Formulæ.
Hydrated Nitric Acid . . . . .	HO, NO <sub>5</sub> . . .	NO <sub>3</sub> H.
Nitrate of Potash . . . . .	KO, NO <sub>5</sub> . . .	NO <sub>3</sub> K.
Carbonic Acid . . . . .	CO <sub>2</sub> . . . . .	CO <sub>2</sub> .
Carbonate of Potash . . . . .	KO, CO <sub>2</sub> . . .	CO <sub>3</sub> K <sub>2</sub> .
Bicarbonate of Potash . . . . .	HO, KO, $\frac{1}{2}$ CO <sub>2</sub> . . .	CO <sub>3</sub> KH.
Hydrated Sulphuric Acid . . . . .	HO, SO <sub>3</sub> . . .	SO <sub>4</sub> H <sub>2</sub> .
Sulphate of Potash . . . . .	KO, SO <sub>3</sub> . . .	SO <sub>4</sub> K <sub>2</sub> .
Bisulphate of Potash . . . . .	KO, HO, SO <sub>3</sub> . . .	SO <sub>4</sub> KH.
Tribasic Phosphoric Acid . . . . .	3HO, PO <sub>5</sub> . . .	PO <sub>4</sub> H <sub>3</sub> .
Tribasic Phosphate of Soda . . . . .	3NaO, PO <sub>5</sub> . . .	PO <sub>4</sub> Na <sub>3</sub> .
Ordinary Phosphate of Soda . . . . .	2NaO, HO, PO <sub>5</sub> . . .	PO <sub>4</sub> Na <sub>2</sub> H.
Hydrated Acetic Acid . . . . .	HO, C <sub>4</sub> H <sub>3</sub> O <sub>3</sub> . . .	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .
Acetate of Potash . . . . .	KO, C <sub>4</sub> H <sub>3</sub> O <sub>3</sub> . . .	C <sub>2</sub> H <sub>3</sub> KO <sub>2</sub> .
Acetic Anhydride . . . . .	C <sub>4</sub> H <sub>3</sub> O <sub>3</sub> . . .	C <sub>4</sub> H <sub>6</sub> O <sub>3</sub> or $\left\{ \begin{array}{c} C_2H_3O \\ C_2H_3O \end{array} \right\} O$
Alcohol . . . . .	HO, C <sub>4</sub> H <sub>5</sub> C . . .	C <sub>2</sub> H <sub>5</sub> O.

These illustrations of M. Gerhardt's system are sufficient to show that in certain cases it admits of being happily applied to compounds of inorganic origin as well as to the more complex bodies derived from the department of organic chemistry. The acid sulphates and carbonates are thus assimilated to the neutral salts, and it will be observed that M. Gerhardt adopts the conclusion that the acid in both these families of salts is tribasic, a conclusion which theoretical considerations render probable.

# ADDITIONAL CORRECTIONS IN PART I.

Page	17,	29 lines from the	bottom, for 12'672,	read 13'672.
"	18,	11	"	" 33'52, " 32'52.
"	41,	1	top, " 1'283187,	" 1'293187.
"	50,	11	"	" (95), " (138).
"	77,	4	"	" 2'48, " 2'510.
"	"	5	"	" 0'0882, " 0'0108.
"	113,	14	bottom, " 1'751,	" 1'957.
"	131,	9	"	" <i>refraction</i> , " <i>reflection</i>
"	163,	6	"	" xxvi., " xx.
"	168,	5	top, " 9393,	" 9390.
"	"	18	"	" dele 9153.
"	"	27	"	" 9250, " 9256.
"	175,	18	"	" 21'60, " 31860.
"	222,	23	bottom, " 0'8009,	" 0'8179.
"	223,	8	top, " 0'872,	" 0'8271.
"	225,	14 from bottom of the table	" 4'4   3'3,	" 7'7   7'7.
"	"	13	" 4'7   4'3,	" 9'0   8'1.
"	"	12	" 7'5   6'9,	" 14'4   12'3.
"	"	10	" 11'0   8'6,	" 19'6   12'9.
"	"	9	" 11'0   10'0,	" 21'0   19'8.
"	"	last line of table	" 275   205'0,	" 238   296'2.
"	251,	In the table, place the figures 8'95 13'19 opposite to arseniuretted hydrogen, instead of chlorine.		
"	345,	20 lines from the bottom, for <i>directly</i> ,	read <i>inversely</i> .	
"	349,	12	"	" <i>piece of plate</i> , " <i>pair of plates</i> .
"	"	5	"	" $\frac{E}{E+r} = \frac{1}{1+20} = 0'047$ , read $\frac{E}{\frac{E}{6}+r} = \frac{1}{\frac{1}{6}+20} = 0'047$ .
"	365,	9	top, " 17'48,	read 12'5.

## CORRECTIONS IN PART II.

Page	452,	2 lines from the	bottom, for 76'99	read 79'19.
"	"	1	"	" 79'19 " 76'99.
"	463,	10 and 14	top	" a, " b.
"	"	12 lines from	"	" b, " a. (in both cases.)
"	511,	18	bottom, " II.	" I.
"	546,	15	"	" to 212° but not higher, read but must be kept below 212°.
"	618,	3	top, " 2 CaF + 2 H <sub>2</sub> O, SO <sub>3</sub> = 2 CaO, SO <sub>3</sub> + 2 H <sub>2</sub> F,	read 2 CaF + 2 (H <sub>2</sub> O, SO <sub>3</sub> ) = 2 (CaO, SO <sub>3</sub> ) + 2 H <sub>2</sub> F.
"	652,	15	bottom, " peroxide,	read suboxide.
"	703,	15	"	" after these bodies were found, add in other respects.
"	776,	15	top, " for opaque,	read oblique
"	791,	10	"	" 57'77, read 56'52.



Page 869,	19 lines from the top,	for $2\text{MgO}, \text{SiO}_2 + 2\text{MgO}, 3\text{SiO}_2$ , read $2(\text{MgO}, \text{SiO}_2) + 2\text{MgO}, 3\text{SiO}_2$ .
826,	13	,, $2(\text{Al}_2\text{O}_3, \text{PO}_3) + 5\text{aq}$ , read $2\text{Al}_2\text{O}_3, \text{PO}_3, 5\text{aq}$ .
827,	8	,, $2\text{Al}_2\text{O}_3, 3\text{SiO}_2, 4\text{aq}$ , read $\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{aq}$ .
840,	16	bottom, ,, <i>an acid chloride</i> , read <i>a hydrated chloride</i> .
857,	4	,, 141, read xli.
868,	10	top, ,, <i>protoxalate</i> , read <i>peroxalate</i> .
905,	15	bottom, ,, oo, read o°.
911,	13	,, after grain of, add metallic iron present with form of.
941,	2	,, 56, read 54.
947,	18	top, ,, <i>exhausted</i> , read <i>excluded</i> .
997,	5	,, <i>sulphide</i> , read <i>sulphate</i> .
1020,	16	,, dele to.

NOTE.—Since the paragraph on teroxide of hydrogen (p. 626) was printed, Dr. Andrews has communicated a paper on Ozone to the Royal Society, in which he shows that the compound evolved during electrolysis is not (as Baumert supposed) a compound of hydrogen, but that it is oxygen in the active state, possessing properties identical with those exhibited by electrified oxygen, *vide* p. 448.







	Ordinary Formulae.	Gerhardt's Formulae.
Hydrated Nitric Acid . . . . .	$\text{HO}, \text{NO}_3$	$\text{NO}_3\text{H}$ .
Nitrate of Potash . . . . .	$\text{KO}, \text{NO}_3$	$\text{NO}_3\text{K}$ .
Carbonic Acid . . . . .	$\text{CO}_2$	$\text{CO}_2$ .
Carbonate of Potash . . . . .	$\text{KO}, \text{CO}_2$	$\text{CO}_2\text{K}$ .
Bicarbonate of Potash . . . . .	$\text{HO}, \text{KO}, \text{CO}_2$	$\text{CO}_2\text{KH}$ .
Hydrochloric Acid . . . . .	$\text{HO}, \text{SO}_3$	$\text{SO}_3\text{H}_2$ .
	$\text{KO}, \text{SO}_3$	$\text{SO}_3\text{K}$ .
	$\text{KO}, \text{HO}, \text{SO}_3$	$\text{SO}_3\text{KH}$ .
	$\text{SHO}, \text{PO}_3$	$\text{PO}_3\text{H}_2$ .
	$\text{N}_2\text{O}, \text{PO}_3$	$\text{PO}_3\text{Na}_3$ .
	$\text{N}_2\text{O}, \text{HO}, \text{PO}_3$	$\text{PO}_3\text{Na}_3\text{H}$ .
	$\text{C}_2\text{H}_5\text{O}, \text{H}_2\text{O}_4$	$\text{C}_2\text{H}_5\text{O}_4$ .
	$\text{C}_2\text{H}_5\text{O}, \text{H}_2\text{O}_4$	$\text{C}_2\text{H}_5\text{KO}_4$ .
	$\text{C}_4\text{H}_6\text{O}_4$	$\text{C}_4\text{H}_6\text{O}_4$ or $\left\{ \begin{array}{l} \text{C}_2\text{H}_5\text{O} \\ \text{C}_2\text{H}_5\text{O} \end{array} \right\} \text{O}^2$ .
	$\text{HO}, \text{C}_2\text{H}_5\text{O}$	$\text{C}_2\text{H}_5\text{O}$ .

These illustrations of M. Gerhardt's system are sufficient to show that in certain cases it admits of being happily applied to compounds of inorganic origin as well as to the more complex bodies derived from the department of organic chemistry. The acid sulphates and carbonates are thus assimilated to the neutral salts, and it will be observed that M. Gerhardt adopts the conclusion that the acid in both these families of salts is basic, a conclusion which theoretical considerations render probable.

END OF PART II.

